

Modern Plastics Encyclopedia

TEXTBOOK

DESIGN GUIDE

ENGINEERING DATA BANK

DIRECTORY OF SUPPLIERS

Modern Plastics Encyclopedia

The Encyclopedia is organized into four basic sections, each planned to serve a different need:

1 For broad and general information about materials and processes: The Textbook (pp. 4-462)

What is high density polyethylene? How do antioxidants work? What is stretch-blow molding? These are the types of questions the Textbook is designed to answer.

The Textbook contains 150 articles that provide information in the areas of: Materials, including resins, foams, films, sheeting, alloys; Composites, including laminates, reinforced materials; Chemicals, additives, fillers, property enhancers, and reinforcements; Primary processing, including testing, tooling, and auxiliary equipment; and Fabricating and finishing. Arrangement of articles is in alphabetical sequence by subject within each category. See listing of Contents, p. 2.

2 For systematic guidelines to the meaningful use of plastics properties in material selection: The Design Guide (pp. 463-498)

What are the key steps in choosing a polymer for a plastics application? What is the meaning of "creep rupture strength" and how can this property be related to my design requirements? What are the effects of elevated temperature exposure on electrical properties, for example, or on chemical resistance? These are the types of questions the Design Guide is designed to answer.

The Design Guide provides the conceptual background and the practical considerations involved in making a product that works, and in making it at the lowest cost. Designing products for rigidity and strength under load and selecting materials for elevated temperature performance are covered. Additional sections describe proper use of creep data and the torsion pendulum test. See the Design Guide Subject Index, p. 463.

3 For precise design and specification data on materials and equipment: The Engineering Data Bank (pp. 499-778)

What specific material will meet my service temperature requirements of 200° F. continuous? Is there a transparent plastic that can be used in a mildly alkaline environment? What material would meet Underwriters Laboratories' V-0 rating and also have good weatherability? What types and sizes of RIM equipment are available? These are the types of questions the Engineering Data Bank is designed to answer.

The Engineering Data Bank provides detailed information on properties and characteristics of specific plastics materials, chemicals for plastics, and processing machinery arranged in tabular form, with most products keyed to individual suppliers and trade designations. Listings also are keyed to advertisements containing additional product information. The Machinery specifier gives detailed specifications on more than 3000 machines. See the Engineering Data Bank Subject Index, p. 499.

4 To reach individual suppliers of products and services: The Directory of Suppliers (pp. 779-890)

Looking to locate . . . Someone who sells high density polyethylene in powdered form? Complete extrusion-blow molding systems? Is in your area and can custom injection mold a thermoplastic part? These are the types of questions the Directory of Suppliers is designed to answer.

The Directory of Suppliers lists products and services for more than 4500 companies. Complete addresses, including phone numbers when possible, are given for each company. Boldface listings are keyed to advertisements which offer additional product and services information. See Directory of Suppliers Subject Index, p. 780.

Modern Plastics

Materials 4

- ABS 4
- Acetal copolymer 5
- Acetal homopolymer 6
- Acrylic 7
- Alloys 120
- Alkyd 10
- Allyl 9
- Amino 10
- Cellulosic 13
- Epoxy 14
- Fluoroplastics 15
- Furan 26
- Ionomer 26
- Melamine 10
- Nylon 28
- Phenol-aralkyl 30
- Phenolic 34
- Phenylene-oxide based resin 36
- Poly(amide-imide) 38
- Polyaryl ether 40
- Polybutylene 45
- Polycarbonate 46
- Polyester 49
 - Aromatic polyester 54
 - Thermoplastic polyester: PBT 49
 - Thermoplastic polyester: PET 50
 - Thermoplastic copolyester 50
 - Unsaturated polyester 54
- Polyethersulfone 110
- Polyethylene 59
 - Ultra-high-molecular-weight PE 64
- Polyimide 66
 - Thermoplastic polyimide 66
 - Thermoset polyimide 66
- Polymethylpentene 70
- Polyphenylene sulfide 73
- Polyphenylsulfone 110
- Polypropylene 74
- Polystyrene 78
- Polysulfone 110
- Polyurethane 88
- Polyvinyl and vinyl copolymers 97
- Silicone 102
- Styrene-acrylonitrile 108
- Sulfone polymers 110
- Thermoplastic elastomers 114
- Urea 10

Composites 124

- Coated fabrics 124
 - Polyurethane 124
 - Polyvinyl 125
- Coextruded film and sheet 126
- Decorative laminates 126
- Flexible laminates: packaging 132
- Industrial laminates 134
- Reinforced thermoplastics 140
- Reinforced thermosets 142
- Reinforced thermoplastic foam 144
- Reinforced thermoset foam 144
- Syntactic foam 145

Chemicals, additives, fillers, property enhancers, reinforcements 146

- Antioxidants 146
- Antistatic agents 147
- Biocides 218
- Colorants 150
 - Color concentrates 164
 - Liquid colorants 164
 - Special colorants 166
- Coupling agents 168
 - Silanes 168
 - Titanates 170
- Emulsifiers 220
- Fibrous reinforcements 172
 - Aramid 172
 - Carbon 174
 - Glass 178
 - Hybrids 182
- Nonfibrous property enhancers 186
- Fillers/extenders 184
- Flame retardants 192
- Foaming agents 194
- Fungicides 218
- Heat stabilizers 204
- Lubricants 208
- Mold release agents 220
- Organic peroxides 208
- Plasticizers 212
- Preservatives 218
- Processing aids 220
- Slip agents 220
- Ultraviolet stabilizers 222
- Urethane foam catalysts 226
- Viscosity depressants 220

Primary processing, including auxiliary, tooling, testing 230

- Blow molding 230
 - Extrusion-blow molding 230
 - Injection-blow molding 232
 - Stretch-blow molding 234
- Calendering 237
- Casting of thermoplastics 238
 - Casting of acrylic 238
 - Casting of nylon 240
 - Casting of PP film 242
 - Casting of PVC film 245
- Coating 245
 - Extrusion coating and laminating 245
 - Melt roll coating 248
 - Powder coating 253
 - Transfer coating 254
- Compression molding 256

- Controls and instrumentation 261
 - Extrusion controls and instrumentation 261
 - Injection controls and instrumentation 264
- Extrusion 266
- Fluid-circulating temperature control equipment 276
- Foam processing 284
 - Expandable PS molding 284
 - Extruding thermoplastic foams 288
 - Melt-processible structural foam molding 292
 - Multicomponent liquid foam processing 296
- Heaters 298
- Injection molding 304
 - Injection molding thermoplastics 304
 - Injection molding thermosets 310
 - Coinjection molding 313
 - Multistation rotary machines 316
- Laminating of film 318
- Materials handling 322
- Mechanical forming 326
 - Blanking 326
 - Stamping thermoplastics 328
- Mixing and compounding 330
 - Continuous compounding 330
 - Discontinuous compounding 334
 - Motionless mixers 336
- Plastisol processing 338
- Parts removal 342
- Post-production handling 342
 - Molded parts removal 342
 - Pipe, tubing, and profiles takeoff 344
 - Sheet takeoff 347
- Radiation processing 348
- Reaction injection molding (RIM) 352
- Reinforced plastics/composites processing 354
 - Continuous RP laminating 354
 - Filament winding 356
 - Matched die molding 358
 - Open mold processing 366
 - Pultrusion 368
- Rotational molding 372
- Size reduction equipment 376
- Takeoff 342
- Testing 378
- Thermoforming 382
 - Oriented container forming 394
 - Preform forming 394
 - Solid phase pressure forming 396
 - Scrapless forming 396
- Tooling 398
 - Extrusion dies 398
 - Injection molds 404
 - Transfer molding 408
 - Web impregnation 412

Encyclopedia

October 1978 Volume 55, Number 10A

Fabricating and finishing 418

- Assembly of fabricated parts 418
- Adhesive bonding 418
- Electromagnetic bonding 420
- Friction joining 422
- High frequency sealing/embossing 424
- Magnetic heat-sealing 426
- Mechanical fastening 427
- Thermal sealing/bonding 428
- Ultrasonic assembly 430
- Decorating and printing 432
- Dyeing 432
- Electroplating 432
- Embossing 436
- Flock coating 437
- Hot stamping 440
- In-mold decoration 442
- Painting 444
- Printing 446
- Vacuum metallizing 449
- Machining 452
- Machining with lasers 457
- Slitting and winding 459

Design Guide 463

- A systematic approach to plastics material selection and design 464
- Designing for rigidity and strength under static load 467
- How to use the Creep Chart to design for static load 470B
- Selecting plastics for elevated temperature performance 491
- Dynamic mechanical properties by torsion pendulum 496

Engineering Data Bank 499

- Design data charts 500
- Chemical resistance 500
- Creep 562
- Dielectric loss 580
- Impact resistance 609
- Poisson's ratio 561
- Temperature index 616
- Property charts 640
- Films 640
- Foamed plastics 645
- Laminates 648
- Chemicals and additives charts 652
- Antioxidants 652
- Antistatic agents 657
- Colorants 660
- Flame retardants 673
- Free radical initiators 678
- Lubricants 682
- Optical brighteners 672
- Plasticizers 694
- Stabilizers 705
- Ultraviolet stabilizers 692

- Machinery specifier 717
- Blow molding machines 717
- Compression molding machines 725
- Extruders 731
- Foam molding machines 744
- Injection molding machines 745
- Reaction injection molding machines 772
- Sheet forming machines 764
- Sprayup equipment 775
- Structural foam machines 770
- Transfer molding machines 776

Flammability data and numerical flame spread ratings presented in the Encyclopedia are not intended to reflect hazards presented by the materials under actual fire conditions.

Directory of Suppliers 779

- Custom processors and converters 851
- Fabrics, papers, and reinforcements 811
- Film, sheet, and profiles 798
- Foamed plastics 797
- Instruments and controls 834
- Laminates and reinforced plastics 803
- Machinery and equipment 812
- Modifiers, additives, and fillers 805
- Resins and molding compounds 785
- Specialized services 842
- Supplies 837

MOPLAY 55(10A) 1-890 (1978)

Advertisers' Index 888

Alphabetical Index of Companies and Addresses 863

Reader Service Cards 891

Editor

Joan Agranoff

Technical editors

John L. O'Toole
Dr. Gordon M. Kline

Associate editors

Roland R. MacBride
Frederick Eickelberg

Directory editor

Maria Filos

Production editor

Vickie Truchan

Graphic design

Bob Barravecchia, art director
Emile Troise, associate

Editorial director

Sidney Gross

Vice President - Publisher

Stuart S. Siegel

Officers of the Corporation

Harold W. McGraw, Jr., Chairman of the Board, President, and Chief Executive Officer;
Robert N. Landes, Senior Vice President and Secretary; Ralph J. Webb, Treasurer.

Officers of McGraw-Hill Publications Company

Gordon L. Jones, President; Paul F. McPherson, Executive Vice President; John G. Wrede, Group Vice President; Senior Vice Presidents: Russell F. Anderson; James E. Boddorf, Planning & Development; Ralph R. Schulz, Editorial; Vice Presidents: Denis C. Beran, European Operations; David P. Forsyth, Research; James E. Hackett, Controller; Eric B. Herr, Economics; Thomas H. King, Manufacturing; Robert L. Leyburn, Circulation; John W. Patten, Sales; Edward E. Schirmer, International.



Modern Plastics Encyclopedia is published annually by McGraw-Hill, Inc., 1221 Ave. of the Americas, New York, N.Y. 10020. Executive, Editorial, and Advertising offices, 1221 Ave. of the Americas, New York, N.Y. 10020. Phone: 212-997-1221. Teletype: TWX-710-581-4879. Cable: McGraw-Hill, N.Y. Please mail all circulation correspondence, subscription orders, and change of address notices to: Modern Plastics Fulfillment Mgr., P.O. Box 430, Hightstown, N.J. 08520. Modern Plastics has no connection with any company of similar name. Modern Plastics Encyclopedia printed in U.S.A.

Modern Plastics issued monthly, 1221 Ave. of the Americas, New York, N.Y. Modern Plastics Encyclopedia Issue published as second issue in October. Modern Plastics Encyclopedia is distributed to Modern Plastics subscribers as part of subscription service. Modern Plastics subscription rates (including Modern Plastics Encyclopedia Issue) for manufacturing, engineering, and R & D companies, also government and schools; in the U.S. and its possessions, 1 year \$17.50, 2 years \$25, 3 years \$37; in Canada, 1 year \$21, 2 years \$30, 3 years \$45. Rates for other companies in the U.S. and its possessions: \$20 per year; Canada: \$25 per year. Single copies (except for Encyclopedia Issues) \$3 each. The name 'Modern Plastics' is Registered (R), U.S. Patent Office. Contents copyrighted (C) 1978 by McGraw-Hill, Inc. All rights reserved.

PERMISSIONS: Where necessary, permission is granted by the copyright owner for libraries and others registered with the Copyright Clearance Center (CCC) to photocopy any page herein for the flat fee of \$1.50 per copy of the page. Payment should be sent directly to the CCC. CCC copying done for other than personal or internal reference use without the express permission of McGraw-Hill is prohibited. Requests for special permission or bulk orders should be addressed to Modern Plastics Reprint Dept., 1221 Ave. of the Americas, New York, N.Y. 10020. ISSN 0085-3518/78\$0.00+1.50.

ABS

By S.E. Ball*

Although frequently considered a single thermoplastic material, ABS is in fact a family of more than 15 different groups of engineering materials formed basically from three different monomers—acrylonitrile, butadiene, and styrene.

This basic three-monomer system can be tailored to yield a variety of balance-of-property combinations as needed for a wide spectrum of applications, ranging from telephone housings to camper tops. Each monomer makes its contribution to the final ABS product: acrylonitrile contributes heat resistance, high strength, and chemical resistance; butadiene contributes impact strength, toughness, and low-temperature property retention; and styrene contributes gloss, processibility, and rigidity.

The ABS family includes general-purpose and numerous specialty grades with specific characteristics such as high heat resistance, transparency, flame retardancy, platability, low gloss appearance, and the capability to be foamed.

In its commercial form, ABS is available as color-matched pellets, unpigmented pellets for customer coloring, and in powder form for blending with other polymers such as PVC.

Chemistry and properties

As a polymer, ABS is composed of discrete rubber particles grafted with styrene-acrylonitrile (SAN) copolymer, which are dispersed in a continuous matrix of SAN copolymer. Current production technology encompasses emulsion, suspension, and bulk processes.

Properties of ABS can be varied widely by: 1) changing the composition ratios of the primary monomers, 2) varying morphology, 3) the selective use of a fourth monomer such as alpha-methyl styrene, or 4) blending (or alloying) with other polymers such as PVC or polycarbonate. Properties can be varied even further by blending with other nonpolymeric materials such as glass.

The product variations possible allow considerable freedom in part design and fabrication with adequate toughness, strength, and rigidity for even structural loadbearing applications.

ABS plastics are viscoelastic thermoplastics that are time, temperature, and load (strain) rate dependent. Considerable property latitude is available. Table I shows the range of properties attainable in ABS polymers, alloys with polycarbonate and PVC, flame-retardant grades, and grades containing alpha-methyl styrene. Note that the properties cannot all be obtained simultaneously. For example, compositions with high modulus values usually are obtained with a reduction in impact strength.

Fig. 1 shows the tensile stress/strain behavior of a general-purpose, high-impact material. ABS plastics are charac-

terized by the capability to deform in a ductile manner at low temperatures.

For designing structural loadbearing applications, products where fatigue resistance is required (e.g., chairs), and interference fit configurations are used, it is recommended that a design limit of 0.5% strain not be exceeded. For one-time snap fit designs, a design limit of 1.0 to 1.5% strain is suggested.

Specialty grades

Electroplating grades. Two types of electroplating (or plating) grades are available—general-purpose and high-performance. General-purpose grades are offered for applications where thermocycling performance is not a major factor, e.g., plated faucets, shower heads, and boat mirrors. Higher-performance plating grades have been designed to meet the more severe thermocycling and performance demands of primarily the automotive market. Applications are plated automotive grilles, exterior decorative trim, and headlight and taillight housings.

High-heat grades. Some variety in heat resistance among ABS grades is available. The newest development in this area has been the development of a 230° F. heat deflection temperature grade. Applications include automotive instrument panels and power tool housings.

Flame-retardant grades. A broad range of flame-retardant ABS grades is obtained through the use of either halogenated additives and/or various alloys with PVC. ABS grades meet Underwriters Laboratories requirements for flammability and continuous-use temperature ratings at specified thicknesses. Applications include appliance housings, power equipment housings, electric switch box housings, and television cabinets.

Structural foam grades. Standard and flame-retardant structural foam grades are available. The blowing agent, which decomposes at processing temperatures, can be compounded into the pellet by the ABS manufacturer or mixed with the pellets by the processor. Advantages include large-part molding, high strength-to-weight ratio, low residual strains in molded parts, sink-free parts, and part integration design freedom. Applications include business machines, home enter-

tainment system cabinetry, appliances, industrial machine housings, and building and construction items.

Transparent grades of ABS with up to 80% light transmission are available. Applications include refrigerator crispers trays, toys, and surgical suction pumps.

Processing

ABS plastics are processible by all techniques common to thermoplastics. Injection molding grades can be processed either on ram or screw-injection molding machines with reciprocating-screw machines generally preferred. Stock temperatures of 425 to 525° F. are preferred. Screws with a compression ratio of 2.0 to 3.0 and L/D ratio of approximately 20:1 are recommended. Injection pressures of 10,000 to 20,000 p.s.i. usually are sufficient in the hydraulic unit and a clamp pressure of at least 3000 p.s.i. for each square inch of projected part area is recommended. High chrome steel should be used for the core and cavity of molds to obtain optimum strength and polish characteristics. Since ABS does not normally stick to molds, a draft angle of 0.5 deg. usually is sufficient. To eliminate any possibility of gas or air being trapped in the mold during molding, the entire circumference of each cavity should have venting to prevent gas or air burns at the parting lines. Wherever possible, water lines should be at least 0.375 in. in diameter.

Structural foam ABS can be converted into pipe, sheet, blow molded shapes, or profile applications using conventional single- or twin-screw extruders. Extruded sheet can be thermoformed by the application of heat and pressure/vacuum. Extruded sheet can be embossed or may have a laminate applied as it passes through the calendaring/cooling rolls. The surface laminate can be used to provide weathering protection or to achieve special decorative effects. Extruders incorporating screws with an L/D ratio of 20:1, 24:1, or 30:1 are preferred. To produce a smooth, homogeneous extrudate with ABS, a single-lead, full-flighted, constant pitch screw with a progressively increasing root diameter and a compression ratio of 2:1 or 2.5:1 is recommended. Common stock temperatures for ABS are in the 380 to 450° F. range. To facilitate

Table I: Property extremes for available ABS grades

Property	Maximum	Minimum
Tensile yield strength at 73° F., 10 ³ p.s.i.	8	2.3
Tensile modulus at 73° F., 10 ³ p.s.i.	380	120
Flexural strength at 73° F., 10 ³ p.s.i.	13	3.8
Flexural modulus at 73° F., 10 ³ p.s.i.	400	130
Rockwell R hardness	117	—
Shore D hardness	—	65
Specific gravity	1.22	0.97
Notched Izod impact, ft.-lb./in.	13	2.3
Heat deflection temp., unannealed, at 264 p.s.i., °F.	230	145

* Group Leader-Structures Engineering Laboratory, Borg-Warner Chemicals, International Center, Parkersburg, W.Va. 26101.

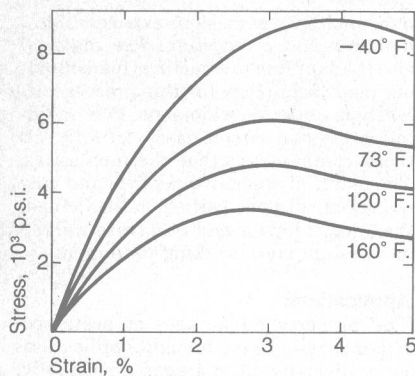


Fig. 1. Tensile stress/strain data for general-purpose, high-impact ABS.

maintaining uniform properties and dimensions across the sheet width, it is normal practice to keep the die cooler than the stock so that a good sheet surface is obtained and to operate end sections of the die at higher temperatures than the center area.

ABS is a mildly hygroscopic material and, consequently, will absorb enough moisture from the air to require drying prior to molding or extrusion. Generally, drying for 2 to 4 hr. at 180° F. is recommended. Hot-air dryers are satisfactory in most cases, but, for best results, de-

humidifying dryers are preferred.

ABS parts can be sawed, cemented, solvent- or ultrasonically welded, hot-staked, hot-stamped, drilled, punched, and riveted. Painting and lacquering should be performed only with ABS manufacturer's recommended systems. Machining characteristics are similar to those of nonferrous metals. In many cases, conventional wood- and metal-working tools are satisfactory although high-speed tools specially designed for work with plastics are available.

Applications

The largest single market for ABS is in pipe and fittings, principally drain, waste, and vent (DWV). In recent years, pipe has accounted for approximately 30% of ABS consumption. While DWV is the largest use, mine pipe and conduit are emerging applications.

Appliances and automotive uses each account for about 15% of ABS consumption, with business machines, communications (telephones), and electrical/electronic applications accounting for another 10%. ABS is the material of choice for refrigerator door and tank liners.

Other applications include luggage, sporting goods, safety equipment, boats, and camper tops. Flame-retardant and expandable grades are finding increased use in business machines, appliances, building components, and institutional products.

for repeated food contact, and a special grade intended for use in low-friction, low-wear applications.

Chemical structure and properties

Acetal copolymer resins are prepared by copolymerization of trioxane with small amounts of a comonomer which randomly distributes carbon-carbon bonds in the polymer chain. These C-C bonds help to stabilize the polymer against thermal, oxidative, and acidic attack. When the polymer is subjected to degradative conditions, such as very high temperatures, depolymerization is stopped short at the C-C link; the copolymer cannot unzip, and it thus possesses a high degree of thermal stability. Hydroxyethyl terminal units, as well as the C-C links in the polymer chain, give the copolymer high resistance to strong alkaline environments.

The short-term strength properties of the copolymer—tensile strength, shear strength, stiffness, and toughness—are all good, but it is the long-term properties of the resin which give it its greatest usefulness. Acetal copolymer is one of the most creep-resistant crystalline thermoplastics. Its unique chemical structure permits it to function without harm in many hostile chemical environments, in a pH range of 4 to 14. It is not harmed by contact with or immersion in common solvents, lubricants, or gasoline. It exhibits good property retention when exposed either to hot air at temperatures up to 220° F., or water as hot as 180° F. for long periods of time. For intermittent use higher temperatures can be tolerated. It has good resilience and fatigue endurance, a low coefficient of friction, and high abrasion resistance.

Acetal copolymer

By M.M. Wilson*

Acetal copolymer resins are strong, hard, highly crystalline thermoplastics. They are true engineering plastics with a unique balance of mechanical, thermal, chemical, and electrical properties. They behave in a predictable, reproducible manner under load and in known environments, and have for many years turned in high levels of performance in demanding long-term applications. Acetal copolymer resins are marketed by Celanese Plastics Co. under the registered trade name Celcon.

Acetal copolymers are available in different grades and formulations, most differing primarily in melt viscosity, though some contain special additives, for instance, ultraviolet stabilizers. Table I lists the most important acetal copolymer compositions currently available, and indicates their principal characteristics and applications. High-melt-strength (low melt index) resins are desirable for processes such as extrusion, extrusion-blow molding, and injection-blow molding. For injection molding, greater flowability is desirable; for this process, the 9-MI material is standard, with the 27-MI grade providing still greater flowability where required. The 25% glass-coupled product is used where maximum tensile strength, rigidity,

and heat deflection temperature are needed.

In its natural color, acetal copolymer is a translucent white. The resin is available in a number of standard colors; also, color concentrates are available for blending with the natural pellets before processing, providing an economical route to colored moldings.

There are grades available that meet FDA standards for applications intended

Specialty grades

Celcon C-300 and C-301 resins are FDA sanctioned for use in articles or components of articles in contact with food where the articles or components are intended for repeated use. Special colors are available that comply with FDA requirements.

Celcon C-245 is a 20% silicone-dis-

Table I: Principal acetal copolymer compounds and their uses

Celcon product	Melt index	Property advantages and applications
U10	1.0	Maximum melt strength. Useful for extrusion of rod and slab, blow molding. Special low-odor grade available for aerosol containers
M25	2.5	Available unlubricated for extrusion of rod, tube, sheet, slab, wire coating. Available lubricated for injection molding of extra-tough parts
M90	9.0	Standard injection molding grade. Available in special UV-stabilized composition for added life in outdoor exposure
M270	27.0	High-flow fast-molding grade. Best performance in multicavity molds for thin-walled parts. Slightly less toughness than 9.0-MI material
GC-25A	—	25% glass-coupled reinforcement. Maximum tensile and stiffness properties. Specially suited for metal-replacement applications

*Group Leader, Celanese Plastics Co., Morris Court, Summit, N.J. 07901.

persed concentrate intended for letdown with general-purpose acetal copolymer. The C-245 blend offers outstanding frictional and wear properties for bearings and moving parts. Also the blend can be used as a processing aid to promote flow and mold release which can result in cycle reduction. For best friction and wear properties, mechanical and physical property balance, a 10:1 letdown ratio of acetal copolymer to C-245 is recommended. As a processing aid, a 40:1 letdown ratio is suggested.

Processing

Acetal copolymers can be processed in all types of injection molding machines, both plunger and screw, though the screw machine is preferred for its better plasticating capability. For maximum flexibility in setting molding conditions, the size of the press selected should be such that the weight of the shot to be molded falls between 50 and 75% of the rated (polystyrene) shot capacity of the press. Clamp tonnage should provide no less than 2 tons, and preferably 3 tons/sq. in. of projected cavity area. The press should be provided with a decompression (suck-back) control to prevent drooling and stringing at the nozzle. Desirable screw

characteristics are: 1) It should be of the metering type, having a number of flights of uniform depth at its front end. 2) It should have a fairly high L/D ratio (about 15:1 minimum) to permit adequate residence time in the barrel. 3) Compression ratio should be no less than 3:1, and preferably 4:1, to assure good mechanical working. 4) Flights in the metering zone should be no deeper than 0.130 in. for screws up to 4 in. in diameter, nor shallower than 0.100 in. for screws down to 2 in. 5) A backflow check valve should be installed on the nose of the screw.

Material temperatures may vary from 360 to 480° F., depending upon cycle time, though most moldings are made in the 360 to 400° F. range. A mold temperature of 200° F. is recommended for most parts, but mold temperatures as high as 250° F. sometimes are used to obtain optimum surface appearance. Injection pressures generally are in the 15,000 to 20,000 p.s.i. range. Acetal copolymers can be ground and remolded many times over with no significant change in processing characteristics or physical properties; after repeated molding, the material darkens progressively.

In addition to injection molding, acetal copolymer can be processed by injection-

blow molding, extrusion, extrusion-blow molding, and rotocasting. The material also is adaptable to structural foam molding, and technology for this process currently is under development. Post-molding processes encompass virtually all those common to other thermoplastics. The material is easily machined and may be sawed, drilled, turned, milled, filed, threaded, tapped, and otherwise worked on standard metalworking equipment.

Applications

The property advantages of acetal copolymer resins have brought applications in a diversity of markets. Principally, these include *plumbing* (valves, pumps, sinks, faucets), *automotive* (electrical switches, body hardware, seat belt components), *toys* (gears and bearings), *pens and pencils* (barrels, tips, springs), *packaging* (aerosol bottles, containers, valves), selective *food contact* applications (meat hooks, milk pumps, coffee spigots), and *industrial* uses (appliance parts, gears, cams, and housings).

A large part of the market for acetal copolymer has been in the replacement of metals, particularly die-cast zinc and aluminum, where it provides improved properties at reduced costs.

Acetal homopolymer

By R.K. Johannes* and J.Y. Dutourt

The chemical structure and high crystallinity of acetal homopolymers result in high value-in-use resins for many applications usually made of metal. Key properties include high melt point, strength and rigidity, good frictional properties, and resistance to fatigue. Acetal homopolymer products retain many of these engineering properties over a wide range of useful temperatures and humidities, as well as solvent exposures. The material is an easily processed thermoplastic designed for injection molding and extrusion. Its high crystallinity makes it possible to mold in short cycles.

Acetal homopolymers are available in compositions to fit a variety of processing and end-use requirements. Table I lists the most important compositions currently available, and indicates their principal characteristics and uses. The three base resins (Delrin¹ 100, 500, and 900) differ primarily in molecular weight, with 100 being the highest. Higher molecular weight increases toughness, but reduces melt flow. All other mechanical properties remain essentially the same.

Chemistry and properties

Acetal homopolymers are high-molecular-weight, stable, linear polymers of formaldehyde, CH₂O. Their good mechanical properties result from the ability of the oxymethylene chains to pack together into a highly ordered crystalline

configuration as the polymers change from the molten to the solid state. All grades contain oxidation and thermal stabilizers to improve resistance to elevated temperature in air and water.

Mechanical. Acetals are the strongest and stiffest of the nonreinforced thermoplastics. Hardness, stiffness, strength, toughness, and resistance to creep and fatigue of the homopolymer are the highest in the acetal family. The 500 resin

has a tensile strength at room temperature of 10,000 p.s.i. and a flexural modulus of 410,000 p.s.i. Fatigue endurance limit is 5000 p.s.i.; at 150° F., 3000 p.s.i.

Tensile and flexural properties are very good so acetal homopolymer resists bending under load. This means that the resin is suitable for some spring applications. Moisture has little effect on mechanical properties and dimensions.

Creep resistance is good: for example,

Table I: Principal acetal homopolymer compounds

Delrin product	Property characteristics and uses
150 SA ^a	High-viscosity unlubricated resin for extrusion. Available in lubricated grade (100) for injection molding extra-tough parts
500 ^a	General-purpose injection molding grade; lubricated. Available in unlubricated grade (550) for extrusion, in a UV-stabilized grade (507), and high-productivity grade (8020)
900 ^a	Injection molding grade with higher melt flow than 500, but somewhat less impact strength and elongation. Available in a high-productivity grade (8010)
8000 ^a	High-productivity, high-flow, fast-molding injection molding grades (8010 and 8020)
570	20% glass fiber-filled 500 base resin for injection molding
500 CL	Low-wear/low-friction. Chemical lubricated wear properties between D500 and AF
AF	Low-wear/low friction. 21% Teflon TFE fluoroplastic fibers. Ultimate in wear properties. Available in extra-tough grade (113) or general-purpose molding grade (313)

^a—Grades with FDA/USDA/NSF acceptable positions.

*Senior Product Specialist and †Product Representative, E.I. du Pont de Nemours & Co., Wilmington, Del. 19898, and Geneva, Switzerland.

¹—Registered trademark of Du Pont Co.

at 115° F. and 1500 p.s.i. stress, strain is less than 1.5% after 10,000 hr. of exposure.

Notched Izod impact strength is essentially constant from -40 to 212° F. Unnotched Izod at 73° F. of the 100 grade exceeds 100 ft.-lb./in.

Chemical resistance. Acetal resin is highly resistant to organic compounds. No common solvents will act on the acetal homopolymer at room temperature, but it is not recommended for extended contact with strong acids or bases outside the range of pH4 to 9.

Dimensional stability. The low moisture absorption of unmodified acetal homopolymer gives it good stability. After equilibrium has been reached at room temperature, parts increase in dimension only 1 mil/in. in going from 0 to 50% relative humidity and 4 mil/in. when totally immersed in water.

Abrasion and frictional resistance. Low wear and low friction of acetal is superior to other thermoplastics and is one of the key reasons the resin is used. Acetal homopolymer exhibits clean-wearing characteristics: particles from the abrading surface generally do not embed in the resin. The nonlubricated coefficient of friction on steel, using the rotating thrust washer test, is 0.1 to 0.3, depending on pressure, and shows little variation from 73 to 250° F.

Electrical. The resin has a low dissipation factor and dielectric constant which prevail over a wide range of frequencies and up to temperatures of 250° F. The polymer maintains its electrical properties under high temperature and humidity exposure and after immersion in water, and retains them on aging. Its nontracking properties serve in special electrical uses.

Burning characteristics. Acetal causes minimal disposal problems because of its clean-burning characteristics, resulting in no generation of smoke.

Specialty grades

The 8010 and 8020 grades are high-productivity resins. The two compositions offer faster material setup, easier ejection from the mold, greater flow, and less warpage than regular grades. The 8010 offers the better flow while 8020 offers the better toughness.

AF resin contains high tensile strength fibers of Teflon¹ TFE fluoroplastic resin; and offers good frictional and wear properties for bearings and moving parts along with minimal slip-stick. It is available in general-purpose and high-impact compositions.

The 500 CL grade offers reduced wear and lower friction through use of a chemical lubricant while maintaining the strength and processibility of standard compositions. Wear and friction performance is between the AF grade and multi-purpose 500 grade.

The 570 grade is a glass-filled product used for higher stiffness, lower creep, higher heat deflection temperature, better arc resistance, and greater dimensional stability, compared to the 500 resin. The glass-filled resin is available

¹—Registered trademark of Du Pont Co.

in natural color and a weatherable black.

All of the basic natural grades of acetal homopolymer comply with a 1976 FDA regulation covering the use of homopolymer in repeated use in contact with food, but not in packaging. This means that the resin can be used in some food-contact applications presently in stainless steel.

Special colors are available that comply with FDA requirements.

Processing

Acetal homopolymers can be melt-processed by injection molding, extrusion, blow molding, and rotomolding. Recently, foam molding has been commercially demonstrated.

The resins are particularly suited to injection molding and extrusion. The acetal homopolymer is not moisture-sensitive, thus it rarely requires a drying step. Fast setup results in minimum problems with nozzle drool and flashing in the mold.

Standard extrusion equipment can be used to produce tubing, rods, slabs, and sheeting.

Semifinished extruded shapes of acetal homopolymer, such as rod and slab stock, are used extensively for the machining and stamping of parts. Stock can be more easily machined than brass with standard brass-cutting tools.

Applications

The high value-in-use of acetal homopolymer is a major reason for its continuing growth in applications traditionally made of metal castings (zinc, brass,

aluminum) and stampings (steel). Cost savings result from elimination of metal assemblies and the reduced number of parts. Many applications use rapid, low-cost plastic assembly techniques such as welding (vibrational, sonic, and spin), snap-fits, and self-threading screws. In the automotive industry, acetal homopolymer is used extensively for components in fuel systems, seat belts, steering columns, window support brackets, and handles.

In the plumbing industry, ballcocks, shower heads, shower mixing valves, flushometer components, and faucet cartridges of the homopolymer are replacing brass and zinc parts. Acetal homopolymer has been used in hot- and cold-water applications during the past 14 years.

Consumer applications take advantage of the hard, smooth feel of acetal, and include handles and other hardware items, the bodies of lighters, replaceable cartridges in shavers, components of better-quality toys, telephone components, lawn sprinklers, garden sprayers, and stereo and videotape cassette components. Zippers and other clothing fittings are large-volume uses.

Machinery applications include mechanical couplings, tabletop conveyor plates, small engine starters, pump impellers, fire-extinguisher handles, and a variety of textile and agricultural machinery components.

Acetal homopolymer rod, tube, and slab are available from several large suppliers. The material is also available from distributors in stock shapes.

Acrylic

Acrylic thermoplastics are characterized by crystal-clear transparency, unexcelled weatherability, and a useful combination of stiffness, density, and moderate toughness. First used in the 1930s for aircraft canopies and windshields, acrylic applications have expanded to include safety glazing, automotive and industrial lighting lenses, diffusers, louvers, solar panels and cells, signs, appliances, displays, sanitary ware, embedment, and dental structures.

Chemistry

Acrylic plastics are made by polymerizing acrylic ester monomers, the most common ester being methyl methacrylate. This monomer is mainly produced by a two-step process: acetone and hydrogen cyanide are reacted to form acetone cyanohydrin which is then reacted with methanol to form methyl methacrylate. A new monomer process involving isobutylene oxidation is being studied by several companies.

Methyl methacrylate monomer is catalyzed to form polymethyl methacrylate. Polymer modifications include

*Product Manager and †Marketing Programs Manager, Acrylic Resins and Monomer, E.I. du Pont de Nemours & Co., Wilmington, Del. 19898.

By D.B. Bivens* and R.B. Rector †

copolymers of methyl methacrylate with other monomers such as methyl acrylate, ethyl acrylate, acrylonitrile, and styrene; and blends with rubber, vinyl, and other modifiers. The polymers are available in the form of sheet, molding and extrusion resins, film, rods, and tubes.

Configurations

Acrylic sheet is made by casting catalyzed monomer between plate glass cells, by casting between moving steel belts, or by extrusion. Cell-cast sheet has had better optical and surface qualities than continuous cast sheet; however, new continuous sheet installations are producing sheet having good optics with low thickness variations. Although cast acrylic sheet has superior optical and surface qualities compared to extruded sheet, continuing improvements in extrusion technology are narrowing the quality differences. Due to manufacturing economics, extruded sheet normally is made in thicknesses up to 0.125 in., cell-cast sheet in a range of 0.03 to 4.5 in., and continuous sheet in a range of 0.06 to 0.375 in.

Abrasion-resistant sheet is produced by coating with polysilicate, giving abrasion resistance up to 75 times that

of uncoated acrylic sheet, plus improved solvent resistance.

Other special grades include mirrorized sheet, ultraviolet screening sheet, and a double-skinned sheet having thermal insulation properties near that of insulated glass.

Acrylic molding and extrusion compounds are produced by three methods: bulk polymerization and solution polymerization, which are followed by extrusion and pelletizing, and by a single polymerization and extrusion process followed by pelletizing.

Molding and extrusion compositions are classified in three ASTM grades based on the fluidity in the melt phase and on the service temperature required in the end use. Those compositions offering highest service temperatures have the lowest fluidity in the melt phase.

Grades 5 and 6 are used for high-flow injection molding applications. Grade 8 is used for extrusion and for molding of parts requiring higher toughness and heat resistance.

Modified acrylics

Three modified acrylics are expanding the range of acrylic applications. Rubber-modified acrylics can be converted to parts having 10 to 20 times the impact toughness of standard acrylics. The rubber-modified acrylics fill the toughness gap between standard acrylics and polycarbonate.

Flame-retardant acrylic/pvc alloys are commercially available in the form of extrusion resin and sheet. The sheet can be thermoformed into shapes having a good balance of toughness, rigidity, cleanability, and impact resistance.

A new multipolymer acrylic molding and extrusion compound is being recommended for food, medical, and pharmaceutical packaging. The multipolymer meets the conditions specified in FDA Regulation 21 CFR 121.2591 for use in food-contact applications, and has good retention of properties after ethylene oxide and radiation sterilization.

Properties

Outstanding acrylic properties are optical quality and weatherability, accompanied by good chemical resistance, and thermal and electrical properties.

Optical. White light transmission of 92% with haze of 1 to 3%, equaling the clarity of glass.

Weatherability. High weathering resistance over long periods of time. No significant yellowing or change in physical properties. Special ultraviolet filtering grades are used with light sources that emit uv energy.

Chemical resistance. Unaffected by most detergents, cleaning agents, and solutions of inorganic acids, alkalies, and aliphatic hydrocarbons. Not recommended for contact with chlorinated and aromatic hydrocarbons, esters, and ketones.

Toughness. Notched Izod impact strength is 0.2 to 0.5 ft.-lb./in. for molded and sheet products. Impact-modified

grades have higher values. Acrylic parts have some notch sensitivity. Part design should minimize stress concentrations.

Thermal. Heat deflection temperatures range from 165 to 212° F. with a service temperature of 200° F. for most grades. As with most thermoplastics, acrylics have a greater coefficient of thermal expansion than metals.

Electrical. Acrylics are good electrical insulators.

Flammability. Acrylics are combustible, thus fire precautions must be observed in design and end-use considerations.

Processing

Molding and extrusion. Acrylic resins in pellet or bead form can be injection molded or extruded on most commercial equipment. Dry feedstock is important for producing a quality product. The resin normally is dried in a regenerative-type dessicant bed drier with an exit air dewpoint monitor. Single-stage plunger, screw or plunger preplasticating, reciprocating-screw machines, and reciprocating-screw machines with vented barrels may be used to injection mold acrylics provided the machine can deliver melt to the nozzle at 10,000 p.s.i. or more. A static mixer between the barrel and nozzle provides a more homogeneous melt.

A wide range of molding conditions is employed in commercial practice, depending on the formulation being molded, the characteristics of the molding machine, design of the mold, and thickness of the finished part. Temperatures and cycle times must be controlled closely for maximum part uniformity and for parts with good dimensional tolerances. Mold shrinkages range from 2 to 8 mils/in., depending on formulation, part shape, mold design, direction of flow, and molding conditions.

Acrylics can be processed on conventional extrusion equipment. Single-stage, two-stage, or three-stage screws may be used for extrusion. Two- and three-stage screws give better performance both in output and quality of product. Takeoff equipment which can accommodate patterned embossing rolls can be used to impart special finishes, patterns, shapes, and lens elements to the extrudate.

Fabricating sheet, rods, or tubes. Acrylic sheet, rods, and tubes can be cut on most power-sawing equipment such as table, band, and saber saws. Thin unpatterned sheet can be cut by breaking along a scribed line.

Sheet can be machined on standard metal and woodworking machine tools, such as lathes, milling machines, drill presses, shapers, and routers.

Acrylic sheet can be thermoformed over a wide range of temperatures on most conventional thermoforming presses and machines. Extruded sheet can be thermoformed to better definition than cell-cast or continuous-cast sheet, but forming conditions must be closely controlled. All standard two- and three-dimensional forming techniques can be

used successfully. Form detail and depth of draw vary from formulation to formulation but normally are very good. Most sheet materials have elastic memory, and can be reheated and reformed without difficulty.

Tubes can be blow molded into shapes, such as spheres, hexes, cubes, etc.

There are a number of suitable methods for bonding acrylic parts. Solvent cements are adequate for cementing most formulations, although higher-strength, more durable bonds can be made with thickened or polymerizable cements designed specifically for acrylics. Parts can be welded by hot-blade or hot-gas, ultrasonic, or spin welding methods. Parts molded or extruded from beads or pellets can be cut, machined, and bonded using the same techniques as for acrylic sheets.

Applications

Major acrylic end uses include signs, glazing, lighting fixtures, sanitary ware, and automotive lenses.

Cast and extruded sheet are formed and painted to make decorative signs. This application is proof of acrylic weatherability as signs put into service over 10 years ago are still attractive and functional. Impact-modified acrylics are penetrating the sign industry by virtue of their increased breakage resistance.

Acrylic sheet is used for glazing, replacing glass in industrial plants, school buildings, and buildings in high-vandalism areas.

An increase in acrylic glazing use resulted from adoption of safety glazing standard ANSI Z-97.1. This standard requires that a sheet of glazing material withstand impacts from designated weights and drop heights. Applications are in hazardous areas such as storm doors, patio doors, floor-to-ceiling windows, and school uses.

Tinted acrylic sheet can be used to reduce solar heat and air-conditioning loads. Conversely, acrylic sheet and extruded shapes are being used in systems designed to capture solar energy. The need for energy conservation in homes and commercial buildings has led to double glazing where acrylic sheet is used as the secondary thermal barrier mounted either on the inside or outside of windows. Window heat losses due to conduction and air infiltration can often be reduced by over 50%.

Acrylic sheet and injection molded shapes are well suited for indoor and outdoor lighting lenses, diffusers, and louvers. In addition to clarity, weatherability, and resistance to light-source uv radiation, acrylics are light in weight, resist breakage (compared to glass), and provide good control of light diffusion. Acrylic rods and fibers are being used in light piping for special effects and for transmitting light from single sources, examples being automotive dashboard lighting and signal lamp monitoring.

An expanding use for acrylics is in sanitary ware where formed acrylic sheet provides the facing surface. The acrylic sheet is reinforced with polyester/glass

fiber to produce bath fixtures such as vanities, tubs, and shower enclosures. The use of impact-modified extruded sheet also is growing in this area.

Acrylics are used in automotive applications because of weather resistance, gasoline resistance, heat resistance, and ability to reproduce reflex optics. Applications include tail light, parking light, and brake light lenses, instrument panels, nameplates, and dials.

Acrylic film in clear and colored forms is being used as a laminate to improve the appearance and weatherability of plastic, metal, and wood substrates. Current uses include doors, window frames, shutters, boat hulls, and exterior components of recreational vehicles.

An alternative to film lamination is acrylic coextrusion with other thermoplastics. Although this technique still is being perfected, significant cost reductions and/or physical property improvements can be realized if the application is well designed. One example is ABS coextruded with acrylic for lavatory and vanity tops.

Other diverse acrylic uses include appliance panels, knobs, and housings,

display cases, decorative sheet in commercial and residential installations, furniture and lamp applications, boat windshields, aircraft canopies, windows, instrument panels, piano keys, and telephone touch buttons.

Regulations

The use of acrylics in buildings is controlled by various municipal, state, and regional codes. If code provisions do not exist for proposed installations, an analysis of life safety hazards and required fire protection must be made.

Sign applications are controlled by sign and zoning codes. Automotive and highway applications are controlled by the National Highway Transportation Safety Administration through the use of American National Standards Institute and Society of Automotive Engineers standards. Appliance components and materials are approved and listed by Underwriters' Laboratories. Aircraft applications are controlled by Federal Aviation Agency regulations. Mass transit uses are controlled by individual transit authorities and/or Urban Mass Transportation Administration guidelines.

and esters are used. Peroxide levels are generally at 3 phr.

Molding compounds based on diallyl phthalate are the major uses. These compounds range in price from about \$1.94 to \$2.24/lb.

Available grades

Molding grades are available in mineral-, glass-, and synthetic fiber-filled types. Compounds for in-line injection molding equipment have been developed for production of high-quality parts on short molding cycles with no volatile byproducts, since the resin cures by addition rather than condensation polymerization. The molding compounds exhibit good electrical properties under high humidity and high temperature conditions; stable low loss factors, high surface and volume resistivity, high arc and track resistance, and good dielectric strength values up to 190° C. for diallyl phthalate and in excess of 205° C. for the diallyl isophthalate resin.

Processing and applications

Most diallyl phthalate compounds are sold under military specification and are used in critical electrical/electronic applications requiring high reliability under long-term adverse environmental condition. A significant application area is electronic connectors in communications, computer, and aerospace systems. Other uses are insulators, potentiometers, and circuit boards.

Arc track and flame-retardant compounds. The ability of a material to resist the formation of a conductive carbon track when a contaminated surface is subject to electrical stress is now a recognized characteristic of electrical insulation. Poor performance in this respect accounts for many electrical failures in switches, circuit breakers, standoff insulators, and TV components. Diallyl phthalate compounds for such applications show promise of optimizing both flame retardance and contaminated arc track resistance.

Reinforced plastics. Allylic resins can be preimpregnated in glass cloth and roving. Applications include tubing, ducting, radomes, junction boxes, and aircraft and missile parts.

Decorative laminates. Diallyl phthalate prepolymer is a versatile surfacing medium for decorative laminates used in furniture and paneling. The monomer is being used with polyester resins to meet the growing demand for economical low-pressure laminates.

Sealants and coatings. Allyl sealants have established themselves in the vacuum impregnation of metal casting, as well as in ceramic and other compositions. Diallyl phthalate is utilized in varnish-like coatings for sealing and other purposes. A recent use is its formulation with carbon to produce conductive elements in precision potentiometers.

The solid free-flowing form of prepolymer and the melting and curing properties of the prepolymer suggest application as powder coatings.

Allylic monomers in polyesters. Allylic

Allyl

The allyl family of esters has as its basis the allyl radical, usually formed from reaction with allyl alcohol. Allyl esters based on mono- and dibasic acids are available as low-viscosity monomers and thermoplastic prepolymers. These find wide utility as crosslinking agents for unsaturated polyester resins and in the preparation of reinforced thermoset molding compounds. Allyl resins can be processed by all modern thermoset techniques.

The resins are notable for their retention of electrical properties under conditions of high temperature and high humidity. Reinforced moldings are characterized by their combination of dimensional stability, chemical resistance, mechanical strength, and heat resistance. Purity of the resin minimizes the possibility of ionic contamination and corrosion of metal inserts.

Allyl molding compounds with flame-retardant additives are commercially available. A number are indexed under the Underwriters' Laboratories recognition program; some being listed at a UL rating of 94 V-0 flammability in very thin sections, along with high arc ignition and track resistance.

Chemistry and properties

Allyls in widest commercial use are the monomers and prepolymers of diallyl phthalate and diallyl isophthalate. These monomers and prepolymers, and combinations thereof, are readily converted into thermoset molding compounds, and

preimpregnated glass cloths and papers. They have found use as sealants for metal casting and show promise in surface coatings.

Shrinkage of allylic monomers during cure is only 12% by volume; prepolymers shrink less than 1%. Other monomers of commercial significance are diallyl maleate, a highly reactive trifunctional monomer containing two types of polymerizable double bonds, and diallyl chloroendate, which is used in flame-resistant compositions.

Diethylene glycol bis(allyl carbonate), CR¹-39 allyl diglycol carbonate, is finding increasing use in colorless, optical castings for eyeglasses because of its impact resistance, light weight, and scratch and abrasion resistance.

Dapon² 35 is the prepolymer derived from diallyl orthophthalate; Dapon M is the isophthalate analogue. These prepolymers are solid, linear, internally cyclized thermoplastic structures containing unreacted allylic groups spaced at regular intervals along the polymer chains.

Allylic homopolymerization is very slow at room temperature and catalyzed compositions can be stored for 1 yr. or more at ambient temperatures with little or no resin advance. Cure rate increases rapidly above 150° C.

A typical catalyst system consists of peroxides (*t*-butyl perbenzoate and dicumyl peroxide are examples) having sufficient thermal stability to persist to completion of the cure. For more critical requirements, dimeric peroxyethers

1—Registered trademark of PPG Industries Inc.

2—Registered trademark of FMC Corp.

*Technical Service Plastic Specialist-Research and Development, Industrial Chemical Group, FMC Corp., Princeton, N.J. 08540.

monomers, principally diallyl phthalate, are used widely in the crosslinking of polyesters in preform or mat binding and laminating prepreg or wet layup; in rope, granular, and premix gunk molding compounds; and in glass cloth and decorative laminates. Diallyl phthalate content of the resin system varies from 10 to 50%. Good handling characteristics and improved properties, although not comparable to those of the prepolymers, account for its use in polyesters.

The low vapor pressure at molding temperatures, 2.4 mm. Hg at 150° C., favors the use of diallyl phthalate over styrene, particularly in larger parts. Because of the low volatility of DAP, allylic

polyesters can be molded at higher temperatures than styrene polyesters and faster molding cycles often can be achieved. Better moldability, including lower mold shrinkage, allows greater freedom of formulation.

Many manufacturers supply diallyl phthalate/polyester as well as uncut polyesters suitable for dilution or dissolving in the monomer. Small percentages of diallyl phthalate are used in combination with styrene in crosslinking of polyester to extend the shelf stability of premix molding compounds.

A relatively new use of DAP monomer is as a catalyst diluent in polyester sprayup application.

Alkyd

Alkyd molding compounds are produced by the mechanical mixing of polyester resins, crosslinking monomers, catalysts, mold release agents, mineral fillers, and fibrous reinforcements. These thermosetting materials are available in three physical forms: granular, extruded, and bulk. The free-flowing granular alkyds are used where impact strength requirements are low. The extruded form is supplied as preweighed logs or continuous rope for medium-impact-strength applications. Bulk alkyd molding compounds are compression molded to produce parts requiring high physical strengths. The good dimensional stability and dielectric properties of alkyds make them especially useful in a wide range of electrical applications.

Chemistry and properties

The major reactive ingredient of all alkyd molding compounds is an unsaturated polyester prepolymer which is formed by the reaction of polyfunctional alcohols with dibasic acids. Also present are an unsaturated monomer and a compound, usually an organic peroxide, which produces free radicals when heated. The application of heat liberates the free radicals which then initiate the crosslinking of the polyester chains by the monomer to produce an infusible, insoluble solid. Alkyd molding compounds utilize a non-volatile crosslinking monomer, normally diallyl phthalate (DAP), distinguishing them from the chemically similar products, commonly called polyester molding compounds, which contain volatile monomers such as styrene or vinyl toluene.

Because of the crosslinking which occurs during cure, alkyds normally exhibit good resistance to creep under load even at elevated temperatures. The degree of unsaturation in the polyester as well as the amounts and types of fillers and reinforcements selected will affect the rigidity and heat resistance of the molded product. Low-shrink additives can be incorporated for improved dimensional control. Mineral fillers generally improve

the surface hardness and electrical properties of alkyds. Hydrated alumina is especially useful since it increases both the arc tracking resistance and the flame resistance of compounds. Glass fiber and other fibrous materials impart additional physical strength.

The specific gravities of alkyd molding compounds range from about 1.60 to 2.30. Most products can be supplied in a wide range of industrial colors. Prices normally are listed in the 40 to 90¢/lb. range.

Specialty grades

The wide range of resins, fillers, additives, and reinforcements available allows a compounder to design products for many specialized applications. Good electrical properties are standard with alkyds, with most exhibiting arc resistance values of over 180 sec. and IEC Track ratings of 500+. Some special products have arc resistance values of greater than 240 sec. and others show superior surface insulation resistance under long-term exposure to high humidity conditions.

Underwriters' Laboratories has assigned alkyds a generic temperature index of 130° C. for electrical and mechanical properties, but some products have

Amino

The amino plastics are a group of thermosetting polymers, produced by reacting an amino containing compound, generally melamine or urea, with formaldehyde. They have found extensive application in molding compounds, industrial and decorative laminates, bonding, paper and textile treating resins and for the manufacture of protective coating and insulating foams.

Available as liquid or dry resins and as filled molding compounds, they are of relatively low molecular weight and can

been recognized for continuous use at 180° C. A number of alkyds have merited a UL94 V-0 flame rating in thicknesses of 1/32 in. or lower. Alkyds are qualified under several MIL-M-14G specifications.

Processing

The physical form in which a given alkyd molding compound is supplied determines the processing methods which can be utilized. Both the granular and extruded forms can be compression, transfer, or injection molded. The granular products normally require a preforming operation for compression or transfer molding, but they are particularly well suited for automatic injection molding. The extruded materials require specialized machinery to be injection molded since they are not free-flowing and cannot readily be fed by a continuous process. The bulk products normally are restricted to compression molding applications in order to make use of the high physical strengths obtainable from this method.

Since alkyds cure quite rapidly at the normal mold temperatures of about 300 to 375° F., fast-acting presses are required to produce well-densified parts. Preheating to 150 to 200° F. greatly improves the flow properties and lowers the required cure time of alkyds. Well-polished, chromed molds are required for consistently good release and glossy part surfaces. In addition, it is necessary that the molds be well vented in order to prevent undensified or undercured areas caused by entrapped air.

Applications

Alkyds typically are used in applications requiring good electrical insulating and/or arc track resistant properties in combination with good mechanical and thermal performance. Thus alkyds find use in automotive parts such as distributor caps, ignition coil towers, and brush holders. In the area of electrical distribution and control, alkyd uses include circuit breakers, switch parts, and transformer housings. Alkyds also are used in a wide range of appliances, as well as in many nonelectrical applications.

By W.H. Fried†

be readily converted to insoluble and infusible end products. Cure ordinarily is effected under the influence of heat, or heat plus acidic catalysts, although properly catalyzed urea resins can be cured without the application of heat.

In the cured state they are essentially colorless and exhibit a high degree of translucency. Additionally, they exhibit a lustrous surface that is hard and mar-resistant and has a high heat deflection temperature, and good electrical arc and track resistance. Melamine-based resins have the added characteristic of high water resistance, as well as resistance to weak acids, strong alkalis, and solvents.

*Technical Group Leader, American Cyanamid Co., 12600 Eckel Rd., Perrysburg, Ohio 43551.

† Technical Manager-Thermoset Molding Compounds, American Cyanamid Co., South Cherry St., Wallingford, Conn. 06492.

These resins also are flame retardant.

Urea and melamine resins sometimes are combined to achieve a balance of cost performance properties.

Most raw materials for the amino resins are not petrochemically derived.

There is an increasing demand toward materials for use in current carrying devices that can withstand higher electrical loads in excess of 600 v. by the comparative tracking index. These requirements have put urea formaldehyde based molding compounds into a preferred position in the wiring device market.

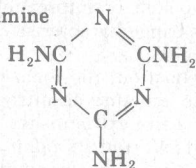
Public demand for insulation materials has established broader markets for urea resin foams in renovation of residential homes. New crosslinking agents for industrial finishes which provide good adhesion and corrosion resistance are on the market.

Chemistry and properties

Urea



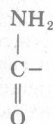
or melamine



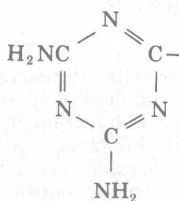
combine with formaldehyde, HCHO spontaneously to form through addition, methylol derivatives:



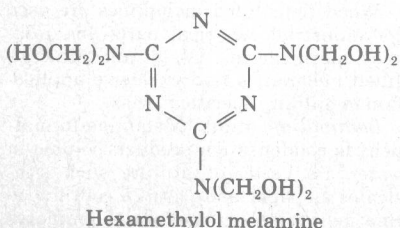
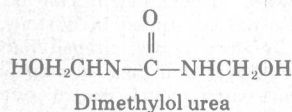
where R represents



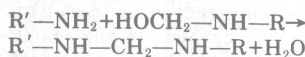
or



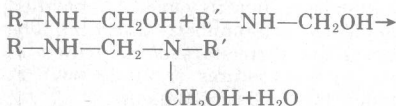
With urea, mono and dimethylol urea are the dominant species. Up to six formaldehyde molecules can react with melamine.



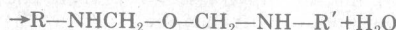
The monomeric resin can react with amino hydrogen and split off water (1) through a methylene bridge condensation reaction. This reaction causes the resin to set to an infusible and insoluble network polymer through the elimination of one mole of water from each methylol linkage:



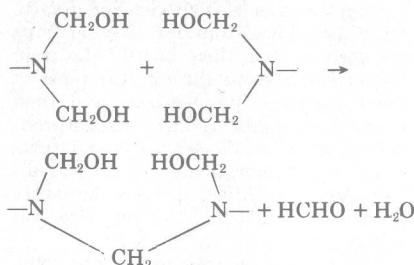
or



2) or an ether bridge formation



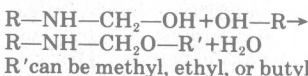
3) or the elimination of one mole of water and one mole of formaldehyde between two methylol groups:



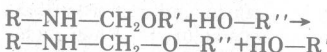
These reactions are controlled by mole ratio, pH, temperature and time. Final cure of the liquid resins at room temperature is triggered by lowering the pH with an acidic catalyst. In molding compounds and laminating resins, heat and pressure are also required.

These resins are commercially available for laminating and bonding and are used in the preparation of molding compounds by compounding with various fillers, catalysts and pigments.

In the production of coating resins another reaction, the preparation of organic, solvent soluble resins or alkylation is important.



Alcohol displacement occurs during the crosslinking reaction of amino resin in modified alkyd baking enamels.



Grades and processing

Molding compounds. Both melamine and urea are used in the manufacture of amino molding compounds. Chemically purified alpha cellulose fibers or a variety of other fillers are used to impart strength and moldability, improve dimensional stability, and reduce molded-in stresses. Clarity and absence of yellow permit the manufacture of colors ranging from light to dark, pastel to high chromatic, and translucent to opaque.

Urea and melamine formaldehyde molding compounds may also contain as

fillers minerals, glass, chopped cotton flock, and wood flour, each selected to impart a particular characteristic.

Molding becomes more difficult and appearance, especially color range, poorer with fillers other than the alpha cellulose.

Phenol-melamine co-reacted molding compounds are commercially available for limited, specific applications.

A liquid resin of specified mole ratios is reacted at closely controlled pH and temperature, mixed with shredded alpha cellulose and dried until the moisture is reduced to 1 to 2% and the resin is advanced to the desired stiffness.

The product is usually ball milled or passed through hammer mills to dispense pigments, lubricants, catalysts and modifying agents. Most of the powder is agglomerated by means of combining rolls, Banbury mixers, and briquetting- or extrusion-type equipment.

The alpha cellulose-based plastics normally are offered in granular form although powder is used in limited applications. They are available in a wide range of flow, stiffness, and rate of cure. Most commonly they are molded by the compression process, in flat bed or rotary presses. Some types can be transfer molded. Special formulations have been developed for the screw-injection and cold manifold injection molding processes.

Molding temperatures for ureas vary from 260 to 340° F.; temperatures as high as 360° F. may be used with melamines. Compression molding pressures vary from 2000 to 8000 p.s.i. on the projected area of the molding. In transfer and injection molding, pressures up to 20,000 p.s.i. are required to move the material rapidly into the mold.

Amino molding compounds, because of their high polarity, can be rapidly and uniformly preheated by high-frequency equipment. Melamine may be preheated to temperatures of 200 to 250° F. while urea, requiring more critical controls, generally is not preheated. Preheating shortens the molding cycle, and imparts a much glossier, smoother surface appearance.

Molded melamine parts are decorated with paper overlays or foils impregnated with melamine-formaldehyde resin, which are placed on the semicured part and cured in the mold. The design of the foil becomes an integral part of the molding. Less-permanent decorating is achieved using color transfer methods and silk screen, pressure-sensitive labels.

Urea molding compounds provide moldings with good surface durability and hardness. Parts are break- and chip-resistant, have good torque retention, are heat-resistant, and do not generally support combustion. They have good rigidity and loadbearing strength, resist organic solvents and have good electrical arc and track resistance. They produce a glossy, smooth molded surface. The melamine-based alpha cellulose-filled compounds exhibit all the properties inherent to urea, some to a more pronounced degree. Resistance to combustion is higher and moldings will not be affected by a

lighted match. Properly cured moldings are not attacked by weak acids, alkalis, or solvents nor by water.

Laminating resins. All laminating resins made with amino resins are based on melamine. Hardness, clarity, stain resistance, and freedom from yellowing make melamine-formaldehyde resin the preferred material for furniture, counter-tops, and other working surfaces that must be both decorative and functional.

Manufacturers of high-pressure decorative laminates frequently prepare the resin syrup, as needed, either from raw materials or by dissolving a spray-dried melamine resin in water. The basic laminating resin generally consists of two moles of formaldehyde to one of melamine. With proper reaction, kettle cycles and pH control of approximately 8 to 10, a stable resin can be manufactured having a 60 to 65% solids range. This resin may be used as such or spray-dried for longer shelf life. Catalysts or plasticizers may be added to promote the cure and flexibility on postforming.

Adhesives and bonding. Both urea and melamine are used in making amino resin adhesives. Melamine is more costly, but gives a more durable glue line. It is also waterproof and therefore used for exterior and marine application. Frequently, a balance between cost and performance is met by combining melamine and urea in the same adhesive formulation. Because the amino adhesives are light colored, they can be used to apply fancy veneer to plywood without discoloration by bleed-through. Large woodworking plants can manufacture their own amino resin adhesives as needed, thereby reducing cost and avoiding problems of storage stability.

Liquid or spray-dried resins are used. Formaldehyde to urea mole ratio varies from 1.5 to 2.0 while up to 3 moles of formaldehyde are reacted with melamine. The reaction is arrested when up to 50 to 60% solids are achieved.

The typical urea adhesive is reacted at pH of 7.5 to 8 at reflux of up to 8 hr. The pH is then lowered to increase the viscosity and advance the resin. When the end point is reached the pH is raised to about 8.0 with caustic soda to retard the reaction and render the resin stable. The liquid urea resins are usually mixed with fillers, such as pecan or walnut shells, wood flour or a combination containing an acid catalyst for use in cold pressing operation. Pressures vary from mere contact to a maximum of 200 p.s.i. The pressure period at 70° F. may be as long as 24 hr.

Urea resins modified with furfural alcohol produce cured glue lines that are more resistant to cracking and crazing and better gap fillers. They are mainly used for furniture assembly or bonding decorative laminate to substrates.

Low shrinkage, craze-resistant urea adhesives, capable of forming thick glue lines, are available as a two-component system—liquid resin and powdered hardener. The hardener contains a catalyst, such as ammonium salts, and a pH buffer, such as tricalcium phosphate, in-

timately mixed with wood and walnut shell flour.

Melamine resins and melamine-urea resins are usually used without external catalyst and are hot-pressed to obtain a cured glue line.

Once mixed with catalyst, all adhesives and bonding resins exhibit limited working life. Therefore, processing steps have to be closely controlled. In the manufacture of plywood the thoroughly mixed resin is applied to the wood or veneer by a glue spreader in closely controlled quantities as a uniform, thin film. The sheets are then stacked and cured at platen temperatures of up to 300° F. under 150 to 200 p.s.i. pressure.

High-frequency gluing commonly is used for curing adhesives in truck flooring and furniture assemblies where the glue line is deeper than 1 in.

Melamine-urea or melamine resins at a minimum of 10% level can be used to bind wood particles, usually in a 40 to 80 mesh range under heat and pressure to form items such as kitchen and dinette seats, school desk tops, etc. Coarser chips are used to form flake board. The resin binder fuses, seeps through the mass of wood particles, polymerizes, and then binds them together. The finished product is harder and denser than the natural wood. It is amorphous, has greater dimensional stability, is more moisture resistant, and has better flexural strength.

Molding pressures of 900 to 2000 p.s.i. on the projected area of the part are normally applied and a 280 to 300° F. mold temperature must be held.

Coating resins. Amino resins for coatings are used in combination with other resinous materials, both natural and synthetic. The amino resin is a minor constituent, and plays the part of a cross-linking agent to join molecules of the other resin into a crosslinked network. To achieve solubility in organic systems, the amino resin is combined with an alcohol such as n-butanol or methanol. Both urea and melamine resins are extensively used in coating systems and the differences mentioned earlier for molding compounds are apparent—ureas have poorer water resistance but cure rapidly, while melamines are higher-cost but give better overall performance. When methanol is used in place of n-butanol, the resin remains soluble in water; resins of this type are used extensively in coatings, and in textile treating from aqueous solution. When melamine is used, and the methylation and subsequent methylation steps are carried to the limit, the product is hexamethoxymethylmelamine which is soluble in organic solvents, and also is compatible with aqueous coating systems. This material is finding extensive use in both organic solvent-soluble and water-soluble coating resin formulations.

Urea formaldehyde foam. Urea adhesive resins can be polymerized into rigid foams when mixed with water and foaming agents and pumped through a foam generation machine where air is forced into the gun and catalyst is added at a

predetermined rate. The foam comes out of a nozzle and flows into any void space. It sets in 10 to 120 sec. and can be troweled. Condensation reaction occurs in 2 to 4 hr. during which period the foam acquires resilience. Full drying takes place in 1 to 2 days. The process is cold setting without any expansion after the foam leaves the foaming machine; thus voids can be filled completely. Normal shrinkage during drying is 1 to 3%.

The following formulation is typical for this process: 54% urea formaldehyde resin; 38% water; 7% phosphoric acid (75%); 1% foaming agent (quaternary ammonium salt).

The foam is a microscopic-sized cell agglomeration with up to 40% of the cells forming capillaries to the outside. It may contain up to 99% air. Care must be taken to obtain complete polymerization and avoid the presence of residual free formaldehyde.

Air dried, the foam weighs 0.75 lb./cu. ft., whereas fresh, it weighs over 2.5 lb., the difference being water which evaporates during the condensation and drying period. It is hydrophobic and very difficult to moisten or impregnate with water. Loadbearing characteristics of the foam are negligible.

During combustion, the foam releases a considerable amount of nitrogen gas which acts as a fire extinguisher. It does not burn by itself, and its point of ignition is about 1200° F. In a Steiner tunnel test (ASTM E84-61), the foam exhibits flame spread of less than 25, smoke density of about 5, and fuel contribution of less than 10. Chemical decomposition point is 220° C. and fuel content is 925 B.t.u./board ft. at 0.6 lb./cu. ft.

K factor is from 0.24 to 0.18 and even freshly foamed, it is a good insulator.

Sound absorbent characteristics of the foams are good. Injected in dry walls, the material will reduce sound transmission by 5 to 7 decibels, provided shrinkage does not exceed 3%.

Applications

Molding compounds. Primary applications for alpha cellulose-filled urea molding compounds are in wiring devices (including circuit breakers, wall plates, receptacles), closures, especially cosmetic, electric blanket control housings, toothpaste tube neck inserts, buttons, toilet seats, housings, knobs and handles.

Melamine alpha cellulose-filled compounds are used principally in molded dinnerware, although significant quantities also are consumed in buttons, ash trays, lavatory bowls, utensil handles, electric shaver housings, mixing bowls, appliance components, control buttons, and knobs.

Wood flour-filled melamines are used for industrial electrical parts and military specifications. Glass- and mineral-filled melamines find exclusive application in military specifications.

Laminating resins. Melamine-formaldehyde condensation products soluble in water are used to saturate such substrates as paper and cloth in continuous treating equipment. Industrial laminates

are made by hot-pressing stacks of these sheets.

Decorative laminates are used extensively for counter and table tops. Post-formable decorative laminates can also be made. Melamine print and overlay sheets are used as surfacing materials for a variety of substrates, generally as wall paneling and furniture surfacing.

Low pressure melamine laminating resins (250 to 300 p.s.i.) are used for furniture and vertical wall surfaces.

Adhesives and bonding resins. Both urea and melamine water-soluble resins find application in this field, which represents the largest tonnage outlet for the aminos, primarily for use with wood-particle board, plywood, boat hulls, molded wood waste products, flooring, and furniture assemblies.

The amino resins also are utilized in bonding of glass or mineral fiber mats, in binders for foundry cores and coated abrasive papers, urea-formaldehyde foams, saturants for fortification of plaster of Paris coatings, and for orthopedic casts and bandages. Mixed with wood chips or wood flour and catalysts they are molded into school desk tops and seats, toilet seats, flakeboard, and serving trays or bowls. Urea resins in conjunction with hydrolyzed starches are used for fabrication of paperboard, corrugated cardboard, as well as in construction of multiwall bags.

Coating resins. Cationic urea-formaldehyde and melamine-formaldehyde condensation resins find use in improving wet strength, dry tensile strength, and bursting strength of paper.

Etherified or partially etherified (alkylated) amino resins, particularly methylated melamine resins, are widely used in the treatment of textiles to provide creaseproofing, shrinkage control, stiffening, water repellency, and fire retardance.

Organic-soluble amino resins of the completely etherified type are normally used in solvent-type coatings, although the methylated derivatives can be made compatible with water-based coating systems. The amino component is present in minor amounts in most coating formulations and acts as a crosslinker. Typical applications for the alkyd resin/amino resin systems include automotive and appliance finishes and coil coatings.

Hexamethoxymethylmelamine and its modifications are being used extensively in both organic and water soluble coating formulations for industrial applications, automotive coatings, appliances, and decorative metals.

Urea formaldehyde foam is being used primarily for thermal and acoustical insulation of either new or existing buildings or homes and to a lesser degree in the floral trade to support plant material and retain moisture, and for packaging.

resistant to bases. It dissolves in all common solvents for cellulose esters, as well as in such materials as hydrocarbons and ethers. It is light amber and slightly hazy. It cannot be obtained in crystal-like clears, but is available in many transparent, translucent, and opaque colors.

The plastic is produced in pellet form for molding and extrusion, and in sheet form for fabrication. It has good processibility and is manufactured in special heat-resistant formulations, high-impact formulations, and formulations for use in contact with food. Ethyl cellulose is tough and moderately flexible, and its outstanding feature is its toughness at low temperatures.

Resins, waxes, and oils often are used to modify the properties of ethyl cellulose for special uses. It must be dried before it is processed.

Ethyl cellulose is useful for flashlight cases, fire extinguisher components, and electrical appliance parts.

Cellulose triacetate

The organic cellulose esters are prepared by reacting chemical cellulose with organic acids and anhydrides, using sulfuric acid as a catalyst in most processes. In the standard synthesis, the reaction proceeds with acetic acid and acetic anhydride to the triester—cellulose triacetate. It has an acetyl content of 43%.

Like cellulose itself, cellulose triacetate plastic must be processed in solution because its very high softening temperature is not greatly reduced by plasticizers. A mixture of methylene chloride and methanol is the commonly used solvent.

Thin sheeting and film are made from triacetate by casting or extruding a viscous solution and evaporating the solvent. Solvent casting is almost always used, however, and can produce thicknesses of less than 1 and up to 20 mils. The sheeting and film have good gage control; the film is grainless and has good optical clarity. Cellulose triacetate products have good dimensional stability and resistance to water, good folding endurance and Mullen burst strength, and little tendency to change on aging. Highly resistant to grease, oils, and most common solvents such as acetone, these materials also have good heat resistance and a high dielectric constant. Triacetate sheeting and film are readily punched, creased, folded, and pressure formed. Neither vacuum forms well.

Applications for cellulose triacetate include visual aids, graphic arts, greeting cards, photographic albums, and protective folders. It is used for such electrical applications as coil forms, core and layer insulation, and nonconducting separators. Because of its inherent toughness and high heat resistance, it is used for photographic film base, for motion picture sound tape, and as a release sheet where high gloss is required.

Cellulose acetate, propionate, butyrate

Cellulose acetate is prepared by hydrolyzing the triester—cellulose triacetate—to remove some of the acetyl groups. Plastic-grade cellulose acetate contains

Cellulosic

By R.E. Scales*

Cellulosic plastics are manufactured by chemical modification of cellulose, a naturally occurring polymer available from wood pulp and cotton linters. Cellulose is not a thermoplastic material; it does not melt. Yet it can be made into a fiber (rayon), a film (cellophane), or a thermoplastic. The first cellulose derivative used for a commercial, synthetic thermoplastic—Celluloid, patented in 1869—was a cellulose nitrate. Other cellulose derivatives include one ether—ethyl cellulose, and four organic esters—cellulose triacetate, cellulose acetate, cellulose acetate propionate, and cellulose acetate butyrate. Cellulose triacetate, because of its very high softening temperature, is not considered a true thermoplastic.

Some of the properties that cellulosics in general exhibit are good scuff resistance, high gas permeability, good electrical insulation, medium water-vapor transmission, and good clarity.

Cellulose nitrate

Prepared by direct nitration, cellulose nitrate is generally characterized by its nitrogen content, usually about 11% for plastics. The standard plasticizer in cellulose nitrate is camphor, although other materials can be used.

Cellulose nitrate has good dimensional

stability, low water absorption, and toughness. Chief disadvantages are its flammability and lack of stability to heat and sunlight.

In processing, cellulose nitrate is mixed with a plasticizer, ethyl alcohol, and other solvents needed to form a viscous plastic mass. This mixture is usually worked on milling rolls to remove some of the solvent and then compression molded into large blocks or extruded in rods or tubing in unheated or only slightly heated equipment. The formed product must be aged to allow the solvents to evaporate. Then the blocks are skived to produce sheeting; or blocks, rods, or tubes can be cut into small pieces for machining.

Cellulose nitrate is readily formed into hollow objects. Sheets, rods, and tubing are fabricated into personal accessories, toiletries, and industrial items. The greatest use is as a base for lacquers, cements, and coatings chemicals.

Ethyl cellulose

Ethyl cellulose is made by reacting chemical cellulose with caustic to form caustic cellulose, which is reacted with ethyl chloride to form ethyl cellulose. Plastic-grade ethyl cellulose contains 44.5 to 48% ethoxyl.

The ether group in ethyl cellulose is essentially nonpolar; and ethyl cellulose has the lowest density of all cellulosics. As an ether, it is not as resistant as cellulose esters to acids, but it is much more

*Market Manager, Plastics Div., Eastman Chemical Products Inc., Kingsport, Tenn. 37662.

38 to 40% acetyl. The propionate and butyrate esters are made by substituting propionic acid and propionic anhydride or butyric acid and butyric anhydride for some of the acetic acid and acetic anhydride. Triesters of these two celluloses are of no commercial importance. Plastic grades of cellulose acetate propionate contain 39 to 47% propionyl and 2 to 9% acetyl; cellulose acetate butyrate, 26 to 39% butyryl and 12 to 15% acetyl.

The esters are fused with plasticizer under heat and pressure to produce homogeneous melts that are formed into small rods or strips and cut into cylindrical or cubical pellets about 1/8 in. on a side. Propionate and butyrate are also available as powders.

Tough, strong, stiff, and hard, cellulose esters have almost unlimited color possibilities, can produce articles with high gloss, and can be supplied in formulations that serve for use in contact with food.

Acetate has the highest specific gravity and the lowest processing rate of the cellulose esters. Propionate and butyrate generally are tougher than acetate.

Mechanical properties of the cellulose ester plastics differ with flow. Hard flows have high hardness, stiffness, and tensile strength. As flow becomes softer, these properties decrease and impact strength increases. Propionate is available in harder flows than butyrate. The softer flows of butyrate have advantages in low-temperature impact strength. Butyrate also has good weatherability.

Electrical properties of cellulose ester plastics are similar. All have a high dielectric constant, good dielectric strength and volume resistivity, and a high dissipation factor.

Their chemical resistance is similar as well. Acetate is somewhat less resistant than propionate and butyrate to water and aqueous solutions, but it is slightly more resistant to organic compounds.

Extruded butyrate and propionate sheeting have good gage uniformity, good surface quality and brilliance, and good visual qualities. Available in gages of 0.7 to 250 mils, these materials are very tough, and they have good color stability.

The cellulose esters are readily processed, but propionate and butyrate are generally considered easier to process than acetate. Cellulose acetate sheet has a long shelf life, can be die-cut, beaded, punched, embossed, laminated, slit, and sealed. The sheeting can be formed by all conventional thermoforming methods, and it is available in transparent, translucent, and opaque colors.

Cellulose acetate propionate sheet thermoforms well by vacuum, air-pressure, and mechanical means. It accepts deep draws and has a fast forming cycle. It can be heat-sealed to coated board, metallized, printed, hot-stamped, and embossed.

Cellulose acetate butyrate sheet is readily formed, and it is especially useful for laminating with thin-gage aluminum foil. It also serves particularly well for vacuum metallizing.

Cellulose acetate is widely used to produce extruded tape, premium toys, tool

handles, and electrical appliance housings. It is also widely used in packaging, particularly for blisters, skins, transparent rigid containers, and windows in folding or setup boxes. Other uses include audio-tape base, electrical insulation, write-on pressure-sensitive tape, gold stamped foils, shields and lenses, eyeglass frames, and microfilm.

Cellulose acetate propionate finds wide use in blister packages and formed containers, as well as in displays, lighting fixtures, safety goggles, motor covers, metallized flash cubes, brush handles,

Epoxy

Epoxy resins, which can contain two types of reactive sites—epoxide groups and hydroxyl groups—have a variety of chemical structures; the most widely used, though, are the diglycidyl ethers of bisphenol A (DGEBA) (Fig. 1). These reaction products of epichlorohydrin and bisphenol A can be liquids where "n" is less than 1 or solids with an "n" value greater than 2. This "n" value can be increased to the point where molecular weight is so high that, for all practical purposes, the epoxide groups can be considered insignificant and hydroxyl groups become the crosslinking sites.

Another relatively important class of epoxy resins is the diglycidyl ethers of tetrabromobisphenol A. Their chemistry and structure (except for the presence of the bromine) is like that of the DGEBA. They produce similar mechanical properties with the added advantage of flame retardance. Other types of epoxies include epoxy novolacs based on phenol and formaldehyde or o-cresol, cycloaliphatic epoxies, and resins with a flexible backbone.

Diluents

It sometimes is necessary to reduce the viscosity of the standard workhorse of the epoxy industry, a honey-like liquid DGEBA with molecular weight approximately 380 and a viscosity of about 14,000 cp. Diluents for epoxies can be either nonreactive or reactive. The nonreactive types, e.g., dibutyl phthalate, do not become an integral part of the cured polymer, but act as plasticizers. Reactive types which contain one or more epoxide groups participate in the crosslinking of the resin system; hence they reduce properties to a lesser extent. The commonly used diluents, reaction products of an alcohol and

face shields, and steering wheels.

Skylights, recreation vehicle windows, toys, tape, curtain walls, and small weather shelters are some of the uses for cellulose acetate butyrate. Others include pen and pencil barrels; tubular, skin, and blister packages; steering wheels; decorative plaques; tool handles; and machine guards. Metallized butyrate sheet is used for printed and formed signs and for interior decoration. Outdoor signs are an important outlet for butyrate in heavy gages. Outdoor applications require special weather-resistant formulations.

By S.J. Hartman*

epichlorohydrin, are butyl, cresyl, phenyl and C-8,10, and C-12,14 glycidyl ethers. The diluents usually are used in amounts of 11 to 25% to reduce viscosity to less than 1000 cp. This viscosity reduction makes easier the addition of filler material such as silica and talc and decreases surface tension to produce better wetting properties.

There recently has been considerable concern expressed for the potential hazards inherent in some diluents; current data indicate that the C-12,14 glycidyl ether is the preferable material. Additional tests are being performed to clarify the situation. Efforts also are being made to find new and safer materials.

Hardeners

In order to be useful, epoxies, except for the ultra-high-molecular-weight resins, must be polymerized with or by a crosslinking agent or hardener. The choice of one of the many types of hardeners will determine the properties of the cured polymer. Accordingly, as much care must be given to hardener selection as to the resin. Hardener categories include: modified and unmodified aliphatic and aromatic polyamines, alicyclic polyamines, polyamides and amido-polyamines, acid anhydrides, catalysts, and coreactants.

Aliphatic amines encompass a large class of materials ranging from unmodified diethylenetriamine to modifications with materials such as propylene oxide or adducts of epoxy resins. These hardeners find use in room-temperature applications and produce good overall strength and chemical resistance properties.

Polyamides, by virtue of the volume used, are the most important group of hardeners. Reaction products of fatty acids and aliphatic amines, polyamides are used extensively in coatings and adhesive applications because of their

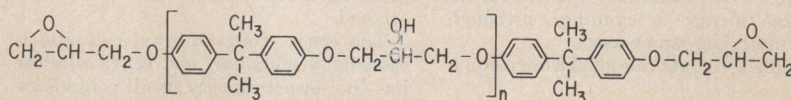


Fig. 1. Chemical structure of diglycidyl ethers of bisphenol A.

* Technical Service Manager-Epoxy Resins, Reichhold Chemicals Inc., P.O. Box 607, Tuxedo Park, N.Y. 10987.

good adhesion, water resistance, long working life, and resiliency.

Acid anhydrides are available both as solids and low-viscosity liquids. In addition to use in electrical applications, epoxy/anhydride systems with long working life, low viscosity, high heat stability and good chemical resistance are especially important in filament winding.

Coreactants such as thermosetting phenolics and urea-formaldehyde resins are important in combination with solid epoxies for use in coatings applications. They coreact with epoxies through hydroxyl rather than epoxide groups.

Applications

Approximately half of the epoxy resins sold find their way into coatings applications. Anticorrosive paints, metal primers, marine finishes, and especially can linings are some of the areas in which they are used.

Increasing interest is evident in the ultra-high-molecular-weight linear epoxies. These resins produce outstanding coatings by solvent evaporation without the use of hardeners, thus affording a one-package system. In addition, with the use of coreactants such as urea-formaldehyde, they result in high-performance baked finishes. The high-molecular-weight epoxies are important in coil coatings, industrial maintenance, metal coatings, primers, collapsible tube finishes, and wire enamels.

Environmental protection and energy requirements are continuing to put pres-

sure on the development of better water-based and high-solids coatings. The latter are being achieved with low-viscosity cycloaliphatic epoxies and a low-viscosity epoxy for weatherable maintenance topcoats.

Epoxy esters are the reaction product of higher-molecular-weight solid epoxies and fatty acids. They are important as metal primers because of their outstanding adhesion. The success of some thermosetting acrylic automotive topcoats is based on the use of an epoxy ester to act as a tiecoat between the acrylic and the metal. A recent development involves a water-reducible epoxy ester which in water phase gives properties approaching those available from solvent-based esters.

Printed circuit board made from laminates of glass fiber cloth and epoxy resin is a large and growing application. Such laminates are produced by impregnating the cloth with a solution of an epoxy resin, usually brominated, catalyzed with a latent hardener such as dicyandiamide. Removal of the solvent produces a stable prepreg from which the printed circuit board is subsequently formed under heat and pressure. A novel and important development involves a formulated resin system to make multilayer laminates and bonding sheets for mass lamination. One system is for fast etchback and a second is for slow etchback to provide laminators with a choice of multilayer laminates of either type.

Epoxies are used as binders for aggregate in the surfacing of floors subjected

to heavy wear and floors in areas where resistance to chemical attack is important. In the decorative field, epoxies, mixed with fillers and marble chips, are used for terrazzo. The resins also are widely accepted in highway applications for patching and sealing of concrete and for skidproof roadway surfaces.

High-strength adhesives are one of the oldest markets for epoxy resins. They may be formulated for curing at ambient or elevated temperature and exhibit exceptionally high-strength bonds to metal, glass, and wood.

Epoxies find considerable use because of their ability to bond to concrete. The bonding of new concrete to old for either repair or remodeling has historically been difficult; epoxies make this bonding possible. The epoxy adhesive is applied to old, clean, sound concrete and the fresh concrete applied before the adhesive cures. The repair of concrete structures damaged with hairline cracks now is being achieved with fast-setting epoxy systems; in this repair the adhesive is applied using pressure techniques.

The potting, encapsulating, and casting of such electrical equipment as transistors, circuits, and insulators provide another outlet for epoxies. Resin/hardener selection is based not only on such standard factors as working life and viscosity, but also resistance to thermal shock. Epoxies provide good dielectric strength and volume and surface resistivity in addition to high mechanical strength properties.

Fluoroplastics

By L.M. Schlanger* and W.E. Titterton †

Fluoroplastics are a family of polymers of general paraffinic structure which have some or all of the hydrogen replaced by fluorine. The family of materials consists of polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP) copolymer, perfluoroalkoxy (PFA) resin, polychlorotrifluoroethylene (PCTFE), ethylene-chlorotrifluoroethylene (ECTFE) copolymer, ethylene-tetrafluoroethylene (ETFE) copolymer, polyvinylidene fluoride (PVDF), and polyvinylfluoride (PVF).

This family of polymers offers unique performance characteristics. Within it are materials which will function in a wide variety of chemical environments, materials useful at temperatures as low as -200 and as high as 260° C., materials with outstanding electrical insulation properties, materials with unique non-adhesive properties, and materials which will pass stringent flammability tests even in thin sections. Most fluoroplastics are totally insoluble in common organic solvents and are unaffected by reactive chemicals such as hot concentrated acids and bases. Some fluoroplastics have useful mechanical properties at cryogenic temperatures and most can be exposed to

high temperatures, 150° C. and higher, without deterioration of mechanical or electrical properties. As a family of polymers, they have low dielectric constants, good power factors, and high volume and surface resistivity. Since the coefficient of friction of fluoroplastics, especially perfluorinated types, is lower than most other substances, these polymers exhibit unique nonadhesive properties. Most fluoroplastics have oxygen indices greater than 30; thus products made from them will not support combustion in air or propagate flame when ignited.

The unique properties of fluoroplastics result in their use in many demanding applications including linings for chemical process equipment, ranging from

valves, pumps, pipe, and fittings to large process vessels, insulation for high-temperature wire and cable as well as sockets, pins and connectors, coatings for home cookware, flame-retarded laminates for aircraft interiors and numerous mechanical seals, rings and bearings on industrial equipment, farm machinery, and passenger vehicles.

Prices of the fluoroplastic resins are given in Table I.

Polytetrafluoroethylene

PTFE is a fully fluorinated polymer made by free radical initiated polymerization of tetrafluoroethylene, a nontoxic gas which boils at -76° C.

The molecular structure of PTFE con-

Table I: Prices of fluoroplastic resins

Resin type	Molding and extrusion resins, \$/lb.	Coating resins, \$/lb.
PTFE	3.75-5.25	4.50-7.00
FEP	6.50-8.00	19.00-25.00
PFA	12.00-14.00	32.00-35.00
PTFE	9.00-25.00	Not available
PCTFE	8.00-10.00	11.00-20.00
ETFE	8.00-10.00	19.00-23.00
PVDF	4.50-5.75	4.50-12.50
PVF	Sold only as film at \$5.00-\$9.00/lb.	

*Marketing Manager-Fluoropolymers and †Manager-Fluoropolymers Technical Service, Allied Chemical Corp., Specialty Chemicals Div., P.O. Box 1087R, Morristown, N.J. 07960.

sists predominantly of linear chains having $-CF_2-CF_2-$ repeating units. PTFE is a highly crystalline polymer with a crystalline melting point of 327°C . Density of PTFE is 2.13 to 2.19 g./cc., depending on grade.

PTFE has outstanding resistance to chemical attack and is insoluble in all organics except a few exotic fluorinated solvents. The dielectric constant (2.1) and loss factor of PTFE are low and stable across the broad temperature and frequency range. Impact strength is high, but its tensile strength, wear resistance, and creep resistance are low in comparison to other engineering plastics. Fillers such as glass fibers sometimes are added to improve mechanical properties. PTFE is a relatively soft plastic which feels slippery and waxy to the touch. Coefficient of friction of PTFE is lower than most other substances. PTFE possesses a high oxygen index and will not support combustion in air. On exposure to flame, it decomposes leaving little or no residue. The material exhibits useful properties from cryogenic temperatures up to 260°C .

PTFE is available in a wide variety of powders, as filled compounds, and as a water-base dispersion. Powder grades are utilized for molding and extrusion. Filled compounds are used primarily for molding. Common fillers for the material include glass fiber, bronze, carbon, and graphite. PTFE dispersion is used for coating or to impregnate porous structures such as fabric. In the U.S., PTFE is sold under the Halon trademark by Allied Chemical Corp., the Teflon trademark by Du Pont Co., and the Fluon trademark by I.C.I.

Because PTFE has exceptionally high melt viscosity, it cannot be processed by conventional extrusion or molding techniques. Instead, molding powders are processed by press and sinter methods similar to those used in powder metallurgy. Objects are molded by compressing granular PTFE at room temperature and 2000 to 10,000 p.s.i. to produce a preform. The preform is sintered at 360 to 380°C . Granular PTFE also may be extruded at slow rates in a ram extruder. The ram compacts the molding powder and feeds it to a die where the material is heated above the melting point, shaped, and allowed to solidify. PTFE paste consists of fine-particle-size ($0.2\ \mu$) powder plus a processing aid such as naphtha. Paste can be ram-extruded at or slightly above room temperature. After extrusion, the processing aid is removed by heating above its volatilization temperature. Paste PTFE products may be sintered or left unsintered, depending on the application.

Primary applications for PTFE are components or linings for chemical process equipment, high-temperature cable insulation, molded electrical components, tape, and non-stick coatings. Chemical process equipment applications include linings for pipe, pipe fittings, valves, pumps, and reaction vessels. Wire and cable applications include aircraft hookup wire, lighting fixture wire, appliance

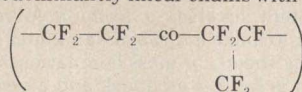
wire, computer wire, and motor lead wire. Molded electrical components include standoff insulators, feed-through insulators, tube sockets, connectors, and insulating bushings. Tape is used as wire and cable insulation and also as pipe thread sealant.

PTFE-filled compounds are used as bushings, rider rings, and seals in compressors; hydraulic applications; automotive power steering and automatic transmissions; and as bearing pads for bridges, pipe lines, and high-rise buildings. Applications for non-stick coatings of PTFE include home cookware, tools, and food processing equipment.

Fluorinated ethylene propylene copolymer

FEP copolymer is made by copolymerization of tetrafluoroethylene and hexafluoropropylene. FEP has most of the desirable properties of PTFE, except that its service temperature is lower, 200°C . Unlike PTFE, FEP can be processed by conventional thermoplastic techniques such as extrusion.

The molecular structure of FEP consists of predominantly linear chains with



structure. The crystalline melting point of FEP is 290°C . Density is 2.15 g./cc.

Like PTFE, FEP is a relatively soft material, which has lower tensile strength, wear resistance, and creep resistance than most other engineering plastics. It is chemically inert and insoluble in all but a few exotic solvents. Dielectric constant is low (2.1) over a wide range of frequencies and temperatures. FEP does not support combustion in air. When exposed to flame, it melts and decomposes. Like PTFE, FEP has good weatherability, and low frictional properties. FEP has useful properties from cryogenic temperatures up to 200°C .

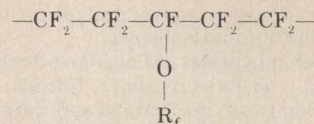
FEP is available as pelletized grades for extrusion and molding and as powders for fluidized bed and electrostatic coating. It also is available as an aqueous dispersion. Semifinished forms of FEP include film, sheet, rod, and monofilament. In the U.S., FEP resin is sold under the Teflon trademark by Du Pont Co.

FEP can be processed by conventional thermoplastic techniques including extrusion, transfer molding, blow molding, and injection molding. Processing equipment should be protected from corrosion by use of alloys such as Hastelloy C, Xaloy 306, or Duranickel.

Applications for FEP are similar to those for PTFE. Important are linings for pipe and chemical process equipment, roll covers, and numerous wire and cable applications including aircraft hookup wire, fire alarm cable, flat cable, and oil well logging cable. FEP film is used as glazing in solar energy collectors.

Perfluoroalkoxy (PFA) resin

Perfluoroalkoxy resins are a new class of melt processible fluoroplastic. The general chemical structure of PFA resin is



where $R_f = -C_nF_{2n} + 1$.

PFA is similar to PTFE and FEP in properties. Like FEP, it can be processed by conventional melt processing techniques. PFA has somewhat better mechanical properties than FEP at temperatures above 150°C .

Like PTFE, PFA resin has the ability to perform at temperature extremes combined with good chemical resistance, low a.c. loss properties, and a low coefficient of friction. Its strength, hardness, and wear resistance are about equal to PTFE and superior to that of FEP at temperatures above 150°C . Its chemical resistance, electrical properties, and coefficient of friction are similar to that of PTFE and FEP. PFA resin has useful mechanical properties from the cryogenic region to 260°C .

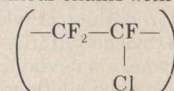
PFA is available as pelletized grades for molding and extrusion and as powders for coating. In semifinished form, PFA resin is available as film and sheet, rod, and tubing. In the U.S., PFA resin is sold under the Teflon trademark by Du Pont Co.

PFA can be processed by conventional thermoplastics techniques, including extrusion, injection molding, transfer molding, and blow molding. Processing equipment should be protected from corrosion by use of alloys such as Hastelloy C, Xaloy 306, and Duranickel.

Applications for PFA include liners for valves, pumps, pipe and fittings, injection molded wafer boats for the electronics industry, heat shrinkable and convoluted tubing, roll covers, and electrical wire insulation.

Polychlorotrifluoroethylene

PCTFE is made by free radical initiated polymerization of chlorotrifluoroethylene. The molecular structure of PCTFE consists of linear chains with



as the predominant repeat unit. PCTFE is a crystalline polymer which melts at 218°C . Density is 2.13 g./cc.

PCTFE is surpassed only by the fully fluorinated polymers in chemical resistance. It is inert to most reactive chemicals. A few solvents dissolve PCTFE at temperatures above 100°C . and it is swollen by a number of solvents, especially chlorinated solvents. It has outstanding barrier properties to gases, especially water vapor. Film made from PCTFE has the lowest water vapor transmission of any transparent plastic film. PCTFE is harder and stronger than perfluorinated polymers; however, its impact strength is lower. Like the perfluorinated polymers, PCTFE will not support combustion in air. On exposure to flame, it melts and decomposes. Electrical properties of PCTFE approach those of perfluorinated