

## ACETAL RESINS

The term “acetal resins” commonly denotes the family of homopolymers and copolymers whose main chains are completely or essentially composed of repeating oxymethylene units  $(-\text{CH}_2-\text{O}-)_n$ . The polymers are derived chiefly from formaldehyde or methanal [50-00-00], either directly or through its cyclic trimer, trioxane or 1,3,5-trioxacyclohexane [110-88-3].

Formaldehyde polymers have been known for some time (1) and early investigations of formaldehyde polymerization contributed significantly to the development of several basic concepts of polymer science (2). Polymers of higher aliphatic homologues of formaldehyde are also well known (3) and frequently referred to as aldehyde polymers (4). Some have curious properties, but none are commercially important.

Formaldehyde homopolymer is composed exclusively of repeating oxymethylene units and is described by the term polyoxymethylene (POM) [9002-81-7]. Commercially significant copolymers, for example [95327-43-8], have a minor fraction (typically less than 5 mol %) of alkylidene or other units, derived from cyclic ethers or cyclic formals, distributed along the polymer chain. The occasional break in the oxymethylene sequences has significant ramifications for polymer stabilization.

Acetal resins were first commercialized by Du Pont in 1960 under the tradename Delrin (registered trademark of E. I. du Pont de Nemours and Co., Inc.) Introduction of the then new engineering plastics followed development of suitable processes for the preparation of high molecular weight formaldehyde homopolymer (5) and for the requisite conversion of the homopolymer's unstable end groups by a procedure known as end-capping (6). Development and commercialization of copolymers of trioxane with cyclic ethers (eg, ethylene oxide) by Celanese (7) quickly followed in 1962. The copolymers did not require end-capping. Rather, good polymer stability could be achieved by ablation of unstable polymer fractions by a suitable process (8). Today there are ten producers of acetal resins, mostly copolymers.

Throughout the remainder of this article the term homopolymer refers to Delrin acetal resin manufactured and sold by Du Pont; the term copolymer refers to Celcon acetal copolymer resins (registered trademark of Hoechst Celanese Corporation).

### 1. Structure and Properties

The many commercially attractive properties of acetal resins are due in large part to the inherent high crystallinity of the base polymers. Values reported for percentage crystallinity (x ray, density) range from 60 to 77%. The lower values are typical of copolymer. Polyoxymethylene most commonly crystallizes in a hexagonal unit cell (9) with the polymer chains in a 9/5 helix (10, 11). An orthorhombic unit cell has also been reported (9). The oxyethylene units in copolymers of trioxane and ethylene oxide can be incorporated in the crystal lattice (12). The nominal value of the melting point of homopolymer is 175°C, that of the copolymer is 165°C. Other thermal properties, which depend substantially on the crystallization or melting of the polymer, are listed in Table 1. See also reference 13.

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**Table 1. Thermal Characteristics of Acetal Resins**

Property	ASTM test method	Homopolymer	Copolymer
heat deflection temperature, °C	D648		
at 1.82 MPa <sup>a</sup>		136	110
at 0.45 MPa		172	158
coefficient of linear thermal expansion × 10 <sup>6</sup> per °C, -40 to 30°C	D696	75	84
thermal conductivity, W/(m.K)		0.2307	0.2307
specific heat, J/(kg.K) <sup>b</sup>		1465	1465
melting point, °C		175	165
flow temperature, °C	D569	184	174

<sup>a</sup> To convert MPa to psi, multiply by 145.

<sup>b</sup> To convert J to cal, divide by 4.184.

The high crystallinity of acetal resins contributes significantly to their excellent resistance to most chemicals, including many organic solvents. Acetal resins retain their properties after exposure to a wide range of chemicals and environments. More detailed data are available (14).

The polymers dissolve in 1,1,1,3,3,3-hexafluoro-2-propanol [920-66-1], hot phenols, and *N,N*-dimethylformamide [68-12-2] near its boiling point. The excellent solvent resistance notwithstanding, solvents suitable for measurement of intrinsic viscosity, useful for estimation of molecular weight, are known (13, 15).

### 1.1. Mechanical Properties

Stiffness, resistance to deformation under constant applied load (creep resistance), resistance to damage by cyclical loading (fatigue resistance), and excellent lubricity are mechanical properties for which acetal resins are perhaps best known and which have contributed significantly to their excellent commercial success. General purpose acetal resins are substantially stiffer than general purpose polyamides (nylon-6 or -6,6 types) when the latter have reached equilibrium water content. The creep and fatigue properties are known and predictable and very valuable to the design engineer.

Typical values of important properties of general purpose acetal resins (homopolymer and copolymer) are collected in Table 2. Properties in the table were determined on specimens subjected only to the conditioning required by the ASTM procedure. In this case, values measured for homopolymer are characteristically higher than those for copolymer.

## 2. Electrical Properties

Electrical properties of acetal resin are collected in Table 3. The dielectric constant is constant over the temperature range of most interest (-40 to 50°C).

### 2.1. Chemical Structure and Properties

Homopolymer consists exclusively of repeating oxymethylene units. The copolymer contains alkylidene units (eg, ethylidene -CH<sub>2</sub>-CH<sub>2</sub>-) randomly distributed along the chain. A variety of end groups may be present in the polymers. Both homopolymer and copolymer may have alkoxy, especially methoxy (CH<sub>3</sub>O—), or formate (HCOO—) end groups. Copolymer made with ethylene oxide has 2-hydroxyethoxy end groups. Homopolymer generally has acetate end groups.

**Table 2. Mechanical Properties of Acetal Resin**

Property	ASTM test method	Homopolymer	Copolymer
tensile strength, yield, MPa <sup>a</sup> , 23°C	D638	68.9	60.6
elongation, break, %	D638	25–75	40–75
tensile modulus, MPa <sup>a</sup> , 23°C	D638	3100	2825
flexural strength, MPa <sup>a</sup> , 23°C	D790	97.1	89.6
flexural modulus, MPa <sup>a</sup> , 23°C	D790	2830	2584
compressive stress, MPa <sup>a</sup> , 23°C	D695	35.8	31
1% deflection		35.8	31
10% deflection		124	110
shear strength, MPa <sup>a</sup> , 23°C	D732	65	53
Izod impact strength, notched, 3.175 mm, J/m <sup>b</sup> , 23°C	D256	69–122	53–80
–40°C		53–95	43–64
water absorption, %	D570		
24-h immersion		0.25	0.22
equilibrium, 50% rh, 23°C		0.22	0.16
equilibrium, immersion		0.9	0.80
Rockwell hardness, M scale	D785	94	80
coefficient of friction, dynamic	D1894		
steel		0.1–0.3	0.15
aluminum, brass			0.15
acetal resin			0.35
specific gravity	D792	1.42	1.41

<sup>a</sup> To convert MPa to psi, multiply by 145.<sup>b</sup> To convert J/m to ft·lb/in., divide by 53.39.**Table 3. Electrical Properties of Acetal Resins**

Property	ASTM test method	Homopolymer	Copolymer
dielectric constant, 10 <sup>2</sup> –10 <sup>6</sup> Hz	D150	3.7	3.7
dissipation factor	D150		
10 <sup>2</sup> Hz			0.0010
10 <sup>3</sup> Hz			0.0010
10 <sup>4</sup> Hz			0.0015
10 <sup>6</sup> Hz		0.0048	0.006
dielectric strength, kV/mm, short time, 2.29-mm sheet	D149	20	20
surface resistivity, ohm	D257	1 × 10 <sup>15</sup>	1.3 × 10 <sup>16</sup>
volume resistivity, ohm·cm	D257	1 × 10 <sup>15</sup>	1 × 10 <sup>14</sup>

The number-average molecular weight of most commercially available acetal resins is between 20,000 and 90,000. Weight-average molecular weight may be estimated from solution viscosities.

The details of the commercial preparation of acetal homo- and copolymers are discussed later. One aspect of the polymerization so pervades the chemistry of the resulting polymers that familiarity with it is a prerequisite for understanding the chemistry of the polymers, the often subtle differences between homo- and copolymers, and the difficulties which had to be overcome to make the polymers commercially useful. The ionic polymerizations of formaldehyde and trioxane are equilibrium reactions. Unless suitable measures are taken, polymer will begin to revert to monomeric formaldehyde at processing temperatures by depolymerization (called unzipping) which begins at chain ends.

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The intrinsic stability of the polymer can be substantially improved by converting unstable hemiacetal end groups to more stable acetate esters in a process, referred to as endcapping, which is routinely practiced with homopolymer. In copolymers, depolymerization proceeds only until a comonomer unit (eg,  $\text{—CH}_2\text{CH}_2\text{—}$ ) is encountered and unzipping stops. Any chemical process which leads to cleavage of the polymer chain or to formation of unstable end groups presages complete destruction of a homopolymer chain. In copolymers, the comonomer units (eg,  $\text{—CH}_2\text{CH}_2\text{—}$ ) add further stability by acting as chain blockers. That is, once a chain is cleaved, the effective length of chain that can unzip is smaller for copolymer. In addition, the greater prevalence of ester end groups in homopolymer reduces their stability in alkaline environments compared to copolymer.

Acetal resins are generally stable in mildly alkaline environments. However, bases can catalyze hydrolysis of ester end groups, resulting in less thermally stable polymer.

Properly end-capped acetal resins, substantially free of ionic impurities, are relatively thermally stable. However, the methylene groups in the polymer backbone are sites for peroxidation or hydroperoxidation reactions which ultimately lead to scission and depolymerization. Thus antioxidants (qv), especially hindered phenols, are included in most commercially available acetal resins for optimal thermal oxidative stability.

Like most other engineering thermoplastics, acetal resins are susceptible to photooxidation by oxidative radical chain reactions. Carbon–hydrogen bonds in the methylene groups are principal sites for initial attack. Photooxidative degradation is typically first manifested as chalking on the surfaces of parts.

Other aspects of stabilization of acetal resins are briefly discussed under processing and fabrication. Reference 15 provides a more detailed discussion of the mechanism of polymer degradation.

When ignited, nonfilled acetal resins burn in air with a characteristic dull blue flame.

### 2.2. Testing

Melt index or melt flow rate at  $190^\circ\text{C}$ , according to ASTM D1238, is the test most frequently applied to the characterization of commercial acetal resins. The materials are typically grouped or differentiated according to their melt flow rate. Several other ASTM tests are commonly used for the characterization and specification of acetal resins.

The weight average molecular weight of acetal copolymers may be estimated from their melt index (MI, expressed in g/10 min) according to the relation

$$\text{MI} = 3.30 \times 10^{18} M_w^{-3.55}$$

The comonomer content of copolymers may be estimated by nmr or by controlled solvolysis of the copolymer followed by quantitative chromatographic analysis of the residues.

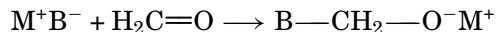
## 3. Manufacturing

Although there is a substantial body of information in the public domain concerning the preparation of polyacetals, the details of processes for manufacturing acetal resins are kept highly confidential by the companies that practice them. Nevertheless, enough information is available that reasonably accurate overviews can be surmised. Manufacture of both homopolymer and copolymer involves critical monomer purification operations, discussion of which is outside the scope of this article (see Formaldehyde). Homopolymer and copolymer are manufactured by substantially different processes for accomplishing substantially different polymerization chemistries.

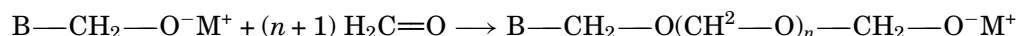
### 3.1. Homopolymer

Formaldehyde polymerizes by both anionic and cationic mechanisms. Strong acids are needed to initiate cationic polymerization. Anionic polymerization, which can be initiated by relatively weak bases (eg, pyridine), can be represented by the following equations:

#### *Initiation*



#### *Propagation*



The exact structure of  $M^+$  and  $B^-$  depends on solvent, the initiator used, and incidental impurities (eg, water).

The anionic polymerization of formaldehyde is free of most spontaneous termination reactions common to free-radical chain growth polymerization of vinyl monomers. Chain transfer to monomer is an intrinsic molecular-weight-regulating reaction and results in one formate and one methoxy end group. Molecular-weight-regulating agents, especially alcohols, are customarily used for optimum control of molecular weight. If an alcohol is used, an alkoxy end group results.

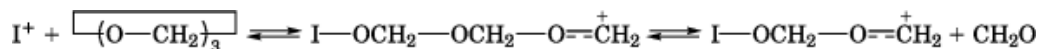
In production, anhydrous formaldehyde is continuously fed to a reactor containing well-agitated inert solvent, especially a hydrocarbon, in which monomer is sparingly soluble. Initiator, especially amine, and chain-transfer agent are also fed to the reactor (5, 16, 17). The reaction is quite exothermic and polymerization temperature is maintained below 75°C (typically near 40°C) by evaporation of the solvent. Polymer is not soluble in the solvent and precipitates early in the reaction.

Polyoxymethylene is obtained as a finely divided solid. The bulk density of the product, which is very important for ease of handling in subsequent manufacturing steps, is influenced by many reaction variables, including solvent type, polymerization temperature, and agitation.

Polymer is separated from the polymerization slurry and slurried with acetic anhydride and sodium acetate catalyst. Acetylation of polymer end groups is carried out in a series of stirred tank reactors at temperatures up to 140°C. End-capped polymer is separated by filtration and washed at least twice, once with acetone and then with water. Polymer is made ready for extrusion compounding and other finishing steps by drying in a steam-tube drier.

## 4. Copolymer

Copolymerization of trioxane with cyclic ethers or formals is accomplished with cationic initiators. Boron trifluoride dibutyl etherate is used in one process. In this case, the actual initiating species is formed by reaction with water (18). Polymerization by ring opening of the 6-membered ring to form high molecular weight polymer does not commence immediately upon mixing monomer and initiator. Rather, an induction period is observed during which an equilibrium concentration of formaldehyde is produced (18, 19).



When the equilibrium formaldehyde concentration is reached, polymer begins to precipitate. Further polymerization takes place in trioxane solution and, more importantly, at the surface of precipitated polymer.

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Comonomer is exhausted at relatively low conversion (20), but a random copolymer is nevertheless obtained. This is because a very facile transacetalization reaction allows for essentially random redistribution of the comonomer units (18) and also results in a polydispersity index near 2.0 (21).

Transfer reactions, analogous to those discussed for homopolymer, also occur during the copolymerization reaction and result in formate end groups.

The enthalpy of the copolymerization of trioxane is such that bulk polymerization is feasible. For production, molten trioxane, initiator, and comonomer are fed to the reactor; a chain-transfer agent is included if desired. Polymerization proceeds in bulk with precipitation of polymer and the reactor must supply enough shearing to continually break up the polymer bed, reduce particle size, and provide good heat transfer. The mixing requirements for the bulk polymerization of trioxane have been reviewed (22). Raw copolymer is obtained as fine crumb or flake containing imbibed formaldehyde and trioxane which are substantially removed in subsequent treatments which may be combined with removal of unstable end groups.

Acetal copolymer may be end-capped in a process completely analogous to that used for homopolymer. However, the presence of comonomer units (eg,  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ ) in the backbone and the relative instability to base of hemiacetal end groups allow for another convenient route to polymer with stable end groups. The hemiacetal end groups may be subjected to base catalyzed (especially amine) hydrolysis in the melt (23, 24) or in solution (25) or suspension (26) and the chain segments between the end group and the nearest comonomer unit deliberately depolymerized until the depropagating chain encounters the "zipper-jamming" comonomer unit. If ethylene oxide or dioxolane is used as comonomer, a stable hydroxyethyl ether end group results ( $-\text{O}-\text{CH}_2\text{CH}_2-\text{OH}$ ). Some formate end groups, which are intermediate in thermal stability between hemiacetal and ether end groups, may also be removed by this process.

Product from melt or suspension treatment is obtained directly as crumb or powder. Polymer recovered from solution treatment is obtained by precipitative cooling or spray drying. Polymer with now stable end groups may be washed and dried to remove impurities, especially acids or their precursors, prior to finishing operations.

## 5. Processing and Fabrication

### 5.1. Finishing

All acetal resins contain various stabilizers introduced by the supplier in a finishing extrusion (compounding) step. The particular stabilizers used and the exact method of their incorporation are generally not revealed. Thermal oxidative and photooxidative stabilizers have already been mentioned. These must be carefully chosen and tested so that they do not aggravate more degradation (eg, by acidolysis) than they mitigate.

Traces of formaldehyde, present in neat end-capped polymer or produced by processing polymer under abusive conditions, detract from polymer stability. Commercial resins typically contain formaldehyde scavengers. Nitrogen compounds, especially amines and amides, epoxies, and polyhydroxy compounds, are particularly efficacious scavengers.

A variety of other additives may be incorporated during finishing extrusion to produce acetal resins especially formulated to enhance certain characteristics for specific applications.

### 5.2. Fabrication

Acetal resins are most commonly fabricated by injection molding. A homogeneous melt is essential for optimum appearance and for performance of injection molded parts. A screw compression ratio of no less than 3:1 is advised and the size of the injection molded shot should be 50 to 75% of the rated capacity (based on polystyrene) of the barrel.

**Table 4. Nonfilled Acetal Resins, General Purpose**

Nominal MI, <sup>a</sup> g/10 min	Hoechst Celanese Celcon	Du Pont Delrin	BASF Ultraform
2.5	M25	100	
9.0 <sup>b</sup>	M90	500	H2320
27.0	M270	900	H2330
45.0	M450	1700	

<sup>a</sup> MI = melt index according to ASTM.

<sup>b</sup> This is perhaps the most commonly encountered melt index.

Acetal resins may also be fabricated into rod, slab, and other shapes by profile extrusion. Extruded shapes are frequently further machined. Parts fabricated by molding or extrusion are amenable to all typical postforming processes.

Reference 27 gives a concise overview of the processing and fabrication of acetal resins.

### 5.3. Scrap and Recycle

Acetal resins can be processed with very little waste. Sprues, runners, and out-of-tolerance parts can, in general, be ground and the resins reused. Up to about 25% of regrind can usually be safely recycled into virgin resin. However, the amount of regrind that can be used in a particular circumstance varies. The appropriate literature from the supplier should be consulted.

Acetal resins are one of several plastic materials specifically targeted for recycle in at least one soon-to-be-constructed recycling facility (28).

### 5.4. Resin Grades

Nonfilled and unmodified (except for stabilizers) grades of acetal resin are generally differentiated on the basis of melt index. Table 4 gives the nominal melt index of various grades of nonfilled Celcon acetal copolymer from Hoechst Celanese. Where possible, the grade of Delrin or Ultraform (registered trademark of the BASF Corporation) that has the most similar nominal melt index is listed. Similarity in MI does not a priori imply that particular resin grades are interchangeable. Standard grades are generally available in a wide variety of colors.

Grades of acetal resins specifically designed to enhance the excellent lubricity of the material, without sacrifice in other properties, are known. These include Delrin AF, Ultraform N2311, and Celcon LW materials. Antistatic grades, particularly useful in electronic applications, have been developed. At least one recently introduced new grade, Celcon SR90, claims good scuff resistance.

Development of toughened acetals has recently flourished. One such grade, Delrin 100ST, boasts a notched-impact strength of 900 J/m (16.86 ft·lb/in.) at 23°C, substantially higher than that of nonmodified, general purpose grades (Table 2).

Glass-fiber-reinforced (increased stiffness and tensile strength) and mineral filled (reduced shrink and warp) grades also have been developed.

## 6. Economic Aspects

Supply and demand statistics for 1988 for all regions of the world as compiled by SRI International are given in Table 5. The world producers of acetal resins and their annual capacities are listed in Table 6 (29). Hoechst Celanese and Ultraform Corporation (a joint venture of Degussa and BASF) have announced capacity

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**Table 5. World Supply/Demand for Polyacetal Resins for 1988<sup>a, b</sup>**

	United States	Western Europe	Japan	Other <sup>c</sup>	Total
capacity	125	116	127	21	389
production	118	100	110	11	339
imports	3	17	4	56–60	80–84
exports	36–41	16	24		79–84
apparent consumption	80–84	101	87	67–71	335–343

<sup>a</sup> Ref. 29. Courtesy of SRI International.

<sup>b</sup> As of October 1989 in thousands of tons.

<sup>c</sup> Includes Mexico, USSR, and Poland.

**Table 6. World Producers of Polyacetal Resins<sup>a</sup>**

Company and plant location	Annual capacity, 10 <sup>3</sup> t
<i>North America</i>	
United States	
E.I. du Pont de Nemours & Company, Inc.	45
Hoechst Celanese Corporation	68
Ultraform Company <sup>b</sup>	12
Mexico	
Du Pont, S.A. de C.V.	1.4
<i>Western Europe</i>	
Germany, Federal Republic of	
Ticona Polymerwerke GmbH <sup>c</sup>	45
Ultraform GmbH	25
Netherlands	
Du Pont de Nemours (Nederland) BV	45
<i>Asia</i>	
Japan	
Asahi Chemical Industry Co., Ltd	30
Mitsubishi Gas Chemical Co., Ltd.	20
Polyplastics Co., Ltd. <sup>d</sup>	77
Korea, Republic of	
Korea Engineering Plastics <sup>d</sup>	10
<i>Eastern Europe</i>	
State Complexes <sup>e</sup>	>10
<i>Total</i>	388

<sup>a</sup> Ref. 29. Courtesy of SRI International as of October 1, 1989.

<sup>b</sup> Joint venture, BASF and Degussa.

<sup>c</sup> Joint venture, Hoechst Celanese and Hoechst AG.

<sup>d</sup> Joint venture, Mitsubishi Gas Chemical and Tongyoung Nylon.

<sup>e</sup> Plants are believed to be located in the USSR and Poland.

expansions in the United States to 77,000 t and 16,000 t, respectively; both were due in place in 1990. Part of general capacity expansion plans, announced by Du Pont for completion in 1991, are believed to apply to acetal resins.

## 7. Specifications and Standards

ASTM D4181 calls out standard specifications for acetal molding and extrusion materials. Homopolymer and copolymer are treated separately. Within each class of resin, materials are graded according to melt flow rate. The International Standards Organization (ISO) is expected to issue a specification for acetal resins before 1992.



Many grades of acetal resins are listed in *Underwriters' Laboratories (UL) Recognized Component Directory*. UL assigns temperature index ratings indicating expected continuous-use retention of mechanical and electrical properties. UL also classifies materials on the basis of flammability characteristics; homopolymer and copolymer are both classified 94HB.

Many grades of acetal are accepted under the component acceptance program of the Canadian Standards Association (CSA) and are listed in the *CSA Plastics Directory*.

The U.S. Food and Drug Administration regulates acetal resins intended for repeated contact with food. The FDA regulation for homopolymer is *21CFR 177.2480* and that for copolymer is *21CFR 177.2470*. The U.S. Department of Agriculture regulates the use of acetal resins in contact with meat and poultry.

The National Sanitation Foundation publishes a list of acetal resins which they find acceptable for use in potable water applications.

Acetal resins are typically supplied in 25-kg multiwall bags and 500-kg Gaylords (rigid containers). Precompounded custom colors are available from manufacturers or the customer may use color concentrates.

## 8. Health and Safety

When processed and used according to manufacturer's recommendations, acetal resins present no extraordinary health risks. Before the use of any plastic material, including acetal, the *Material Safety Data Sheet (MSDS)* applicable to the grade in question should be consulted.

If acetal resins are processed at temperatures substantially above those recommended for the particular grade, minor amounts of formaldehyde may be liberated. Formaldehyde (qv) is a colorless, lacrimatory gas with a pungent odor and is intensely irritating to mucous membranes. The human nose is sensitive to concentrations in the range of 0.1 to 0.5 ppm. The current threshold limit value for formaldehyde is 1 ppm.

## 9. Uses

The mechanical strength, friction and wear characteristics, predictable long and short term properties, and generally excellent solvent resistance of acetal resins make them ideal candidates for industrial applications. Conveying devices and gears are excellent examples of this type of application. Information on the design of such devices is available from suppliers (30). Optimization of design and molding of gears from acetal resins has been discussed in the technical literature (31). Acetal resins compete effectively with nylons and thermoplastic polyester among other resins in many industrial applications.

Molding of parts for a wide variety of plumbing and irrigation applications consumes as much acetal resin as the industrial applications. Rod and slab stock can be machined into components for precision flow control devices.

Acetal resins are also used extensively in transportation, especially automotive. Handles and internal components (gears, gear racks, cables) for window lifts and other similar devices are examples. Most of the applications which do not involve painting or plating are below the window line. Many common consumer items are manufactured essentially entirely from acetal resin (eg, disposable lighters) or have critical components molded from acetal resin (eg, hubs and platforms for videocassettes). The properties that make acetal resins useful in industrial applications make them useful for internal components, especially mechanical drive systems, of many household appliances.

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### Related Articles

Formaldehyde; Plastics testing