CYCLIC OLEFIN COPOLYMERS

Cyclic olefin copolymers are a new family of materials suitable for high-performance optical, medical, electrical, packaging, and other applications.

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Cyclic olefin copolymers (COCs) are engineering thermoplastics with a unique combination of properties. They are proving valuable in fields as diverse as CD-ROM, packaging, medical equipment, optics, capacitors, and toner binders for printers (Fig. 1).

COCs have glass-like transparency, low density, high heat-deflection temperature, and excellent electrical properties (Table 1). They also have high tensile modulus, low elongation at break, high rigidity, and good surface hardness. Beyond this, they are highly pure and have excellent water-vapor barrier properties and low moisture absorption. These materials flow well, and shrink and warp little during injection molding, blow molding, or extrusion.

In terms of chemical properties, they resist aqueous acids and bases, as well as polar organic chemicals. However, they are attacked by aliphatic and aromatic hydrocarbons, and should not be exposed to solvents such as hexane and toluene. Exposure to certain oils and fats should also be avoided.

Literature references to COCs first appeared in the 1950s, and the first commercial COCs, made via Ziegler-Natta catalysis, became available in the late 1980s. Metallocene-based COCs became possible when appropriate metallocene catalysts emerged in the mid-1980s. These catalysts, which foster the linkage of cyclic and linear olefins, enabled large-scale copolymerization of ethylene and norbornene.

The world's first commercial metallocene-based COC plant started up in September 2000 in Oberhausen, Germany, with a capacity of 66 million lb/yr. The plant first reacts ethylene and cyclopentadiene to form 2-norbornene (a bicyclic olefin), which is further reacted with ethylene to form the final polymer.

The COC formed in this process has a carbon main chain and no double bonds (Fig. 2). Norbornene is much bulkier than ethylene, and has a rigid bridged-ring structure that prevents crystallization. This compound is incorporated randomly on the main chain, making the COC structure totally amorphous. Norbornene also stiffens and strengthens the polymer, and increases its glass transition temperature (T_g) in proportion to its incorporation in the chain.

The process is flexible and creates a spectrum of

Fig. 1 — Ticona's Topas cyclic olefin copolymer is being considered for high-resolution CD-ROMs.

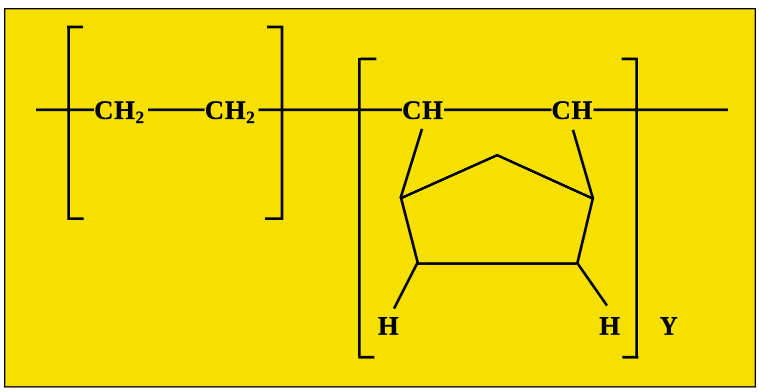

Fig. 2 — COCs are polymerized from ethylene and norbornene groups. Norbornene is incorporated randomly on the carbon main chain.

*Range of properties of commercial COCs**

Physical/Mechanical properties	Value
Density, g / cc	1.02
Water absorption, %	<0.01
Water vapor permeability @ 23°C, 85% R.H., g / m^2 / day	0.02 to 0.04
Tensile strength, psi	9570
Elongation @ break, %	3 to 10
Tensile modulus, kpsi	377 to 464
Charpy impact, kJ / m2	13 to 20
Notched charpy impact, kJ / m^2	1.7 to 2.6
HDT at 66 psi, °C (°F)	75 (167) to 170 (338)
Glass transition temperature °C (°F)	80 (176) to 185 (365)
Melt flow index at 260°C, g / 10 min.	4 to 56, depending on T_g
Mold shrinkage, %	0.6 to 0.7
Optical properties	
Luminous transmission, %	92
Refractive index @587.6 nm	1.533
Abbe number	56
Photoelasticity,: mm^2 / n	6x10^{-7}
Haze, %	1 or below, depending on grade
Birefringence	Low
Electrical properties	
Dielectric const. @ 60 Hz	2.35
Comparative tracking index, volts	>600
Volume resistivity, ohm-cm	>10^{16}
Dielectric breakdown	30 kV / mm
Dielectric loss at 60 Hz	< 0.02 %

** Data encompass Ticona's Topas COC grades 8007, 5013, 6013, 6015, 6017*

properties, depending on the norbornene / ethylene ratio. The higher this ratio, the higher the T_g and heat distortion temperature (HDT). Commercial grades have HDT of 75° to 170°C (167° to 338°F) and T_g of 80° to 185°C (176° to 365°F). Grades with T_g above 100°C (212°F) have a modulus of 3100 to 3300 MPa (450 to 478 ksi), about that of polystyrene (PS). Those with a lower T_g have a lower modulus of elasticity but greater elongation at break. Flowability is adjusted by controlling molecular weight.

In addition to their optical, electrical, medical, and packaging applications, COCs have many other actual and potential uses, such as toner binder resin, housings, powder coatings, foams, and gaseous filter media.

Precision optics

COCs are glass-clear and water-white. Their light transmittance, which extends through the visible spectrum into the near UV, exceeds that of PS and polycarbonate (PC), and nearly equals that of polymethyl methacrylate (PMMA), Table 2. They have low birefringence and low haze. They also have a high Abbé number and low chromatic aberration. The Abbé number is a measure of the change of refractive index with wave length. This number is high for COC, indicating low chromatic aberration.

Compared with other transparent amorphous plastics, they have higher modulus and HDT and are less dense (PC and PMMA are about 20% higher in density). They have less than half the density of glass, and are less brittle, and so can replace glass in optical components wherever weight and / or durability are issues. This includes video camcorders, hard disk drives, flat panel displays, and light guides for automotive and other applications. In addition, injection molded COC optical parts can be significantly less expensive to manufacture than their glass analogs, which may require costly grinding and polishing to meet exact tolerances.

The optical properties of COCs are most like those of PMMA, but they have much better heat resistance and only one tenth of its moisture absorption. They are about 75% stiffer than PC, and have about the same resistance to crack propagation as PMMA or PS. They hold accurate lens shapes better than other clear plastics because of their very low moisture absorption and good creep resistance at higher temperatures. These properties give them advantages in applications such as projection TVs and computer displays, and other applications where heat or humidity can deform acrylic or PC lenses.

These factors, as well as their low birefringence, excellent surface replication, and transparency to blue-green laser light, make them a candidate for new-generation, higher-capacity DVDs. Other potential optical elements include lenses for LEDs, copiers, printers, diffractive optics and lighting, metallized reflectors, and mirrors. They are also suitable for contact lens tooling where optical-quality surfaces are required. Special grades have also been developed to provide clarity and small, relatively uniform particle size in toner binder resin for laser print engines.

Electrical applications

COCs are good electrical insulators, with relatively constant electrical properties over a wide range of temperatures and frequencies. They are nonpolar and have low electron mobility and negligible ionic content. This creates high resistivity and a low dissipation factor that is well below those of PS and polypropylene (PP). The room-temperature dielectric constant of COC is about 2.35, and it diminishes less with increasing temperature than those of PP and other olefinic materials.

These advantages are particularly useful in thin film capacitors. For example, at 120°C, the dielectric loss factor of COC is less than half that of PP. Also, at this temperature a COC film with the same capacitance as one of PP would have 15% less area. COC-based capacitors can thus be smaller and more energy-efficient than those of PP in such applications as AC motor starters and high-frequency semiconductor circuits.

The COC films in capacitors are thin, cast films that undergo biaxial orientation to make them stiffer, stronger, and more ductile. Biaxially oriented COC films as thin as 7 microns exhibit a modulus of elasticity increase of 1.5 times, a tensile strength increase of 2.5 times, and an elongation at break increase of 20 times. COC films are also easily metallized on both sides at once without pretreatment, which improves capacitor fabrication.

Medical applications

COCs are suitable for medical and diagnostic

*Table 2 — Property comparison with other clear plastics**

Property	COC	PS	PC	PMMA
General				
Density, g / cm^3	1.02	1.05	1.2	1.2
Flexural modulus, Msi	0.5	0.45 - 0.5	0.34	0.45
Tensile strength, ksi	9	6.4 - 8.2	9	10
Elongation, %	3 - 10	2 - 4	80	5
Notched Izod, ft-lb / in.	0.4	0.4	5 - 16	0.3
Heat distortion temperature, °C (°F)	75 - 170 (167 - 338)	75 - 94 (167 - 201)	142 (288)	92 (198)
Shore D	89	75 - 84	85	100
Water absorption, %	0.01	0. 1 - 0.3	0.04	0.1
Optical				
Luminous transmission, %	92	91	88	92
Haze, %	1	3	1	1
Index of refraction	1.53	1.59	1.586	1.491
Abbé Number	56	31	34	61
Birefringence	Low	Variable	Variable	Low
Stress-optical coeff., 10^{12} Pa / s	4.0	4.8	68	–4.6

**Data for plastics other than for COC is from literature sources.*

products because of their clarity, moisture barrier, shatter resistance, and chemical resistance. They withstand all common sterilization regimes, including gamma radiation, steam, and ethylene oxide.

They are exceptionally pure and have excellent biocompatibility. Tests show that no substances leach from them within the limits of detection during immersion in water or isopropanol after 24 hours at 70°C (160°F). Ethylene-norbornene COCs comply with U.S.P. Class VI requirements, and have received U.S. Food and Drug Administration (FDA) Drug and Device Master File numbers DMF# 12132 and MAF# 1043, respectively.

Given their better shatter resistance than glass, COCs can replace glass in prefilled syringe bodies, serum vials, blood containers, petri dishes, test tubes, and bottles of various sizes, as well as other diagnostic and biomedical containers. COC cuvettes and multi-well microtiter plates offer resistance to such common polar organic solvents as dimethyl sulfoxide, as well as high light transmission through the near UV. These COC devices provide low haze and low chromatic aberration for sensitive and accurate spectrophotometer readings.

In pharmaceutical bottles, their high moisture barrier can extend drug shelf life longer than commodity plastics, either keeping moisture out or preventing moisture loss during storage. COC resins can also lengthen the life of moisture-sensitive medications in other drug-delivery systems such as injector pens and inhalers.

Packaging applications

COC may be combined with polyethylene (PE) in monolayer blend films or used in multilayer films in flexible packaging for food, drugs, cosmetics, personal care, and consumer products. In blends with PE, they enhance stiffness and sealability. As the core layer in multilayer films, they provide a moisture barrier, clarity, and stiffness.

When up to 25% COC is blended into low-density PE or linear low density PE, film stiffness can increase by as much as ten times with minimal impact on other film properties. This allows the film to be down-gaged for source reduction and lower cost. COCs can lower the haze of PE films when added at low levels, and can also reduce the coefficient of friction and the blocking tendency of such films.

When incorporated in the heat-seal layer of bags or stand-up pouches, they can improve hot-tack and ultimate seal strength without altering the seal initiation temperature of the PE film. Typical uses for these blends include fresh-cut produce bags and pouches for drinks, cereals, candies, soups, and pet foods.

In multilayer structures, laminated and coextruded films are made with a COC core and outer layers of other resins. COCs provide a higher moisture barrier than that available with other common film materials. In fact, they have roughly double the moisture barrier of high density PE, three times that of low density PE, seven times that of unoriented PP, and ten times that of polyvinyl chloride (PVC). The high moisture barrier of COC resins is useful in coextrusions with ethylene vinyl alcohol (EVOH), where it can protect the EVOH layer against loss of oxygen barrier properties due to water absorption.

COC coextruded with PE usually needs no tie

COC benefits and applications

Benefits	Applications
Low density	Electrical: capacitor films
Excellent optical properties, including high transparency and clarity	
Excellent barrier properties	Laboratory, diagnostic and medical: petri dishes, pipettes, graduates, bags, syringes, microtiter plates, contact lens tooling, inhaler and dialysis parts
High dimensional stability	
High heat deflection temperature	
Resistance to acids, bases and polar solvents	
High stiffness, modulus, tensile strength, surface hardness	Packaging: blister packaging, food films, bags and pouches
High purity with very low extractables	
Excellent electrical insulation with low dielectric loss	
Good metallization; able to metallize film on both sides at once with no pretreatment	Optical: lenses, light guides, reflectors, display panels
Wide range of available glass transition temperatures	Other: laser printer toner binder, nonwoven filter media, powder coating, foams
Replicates submicron surface features	
Good processibility, including high melt flow and low shrinkage	

COC-based film forms blisters with more uniform wall thickness.

layer because the two are highly compatible. However, tie layers are generally required in coextrusion of COC with such plastics as PP, PVC, PC, nylon, polyester (PET, PBT, and PEN), and EVOH.

COC-based, multilayer barrier film is processed much like PVC film coated with polyvinylidene chloride (PVdC). For blister packaging, it is thermoformed at relatively low temperatures (110° to 130°C, 230 to 266°F) on existing machinery and with 10% to 20% shorter cycle times than PVC / PVdC film. The COC-based film forms blisters with more uniform wall thickness than those made of competitive materials, and the improved wall uniformity provides a more effective moisture barrier. These COC-based multilayer films are cost competitive with those made of PVC / PVdC.

In a specific example, a five-layer laminated film was thermoformed into blister packs to protect hydrolysis-sensitive tablets from high humidity in a tropical region. This involved a laminated film with a COC core and a thin layer of polypropylene on either side. Diffusion tests showed that the COC-based film had a water vapor permeability of less than 0.1 $g/m^2/day$.

In other packaging applications, COC blends with incompatible polymers such as PET and PP offer improved film frictional behavior and opacity. Monolayer COC blend films have good twist-wrap behavior, and can be easily metallized. COC-based films can be laminated or extruded onto paperboard to provide a good water vapor barrier. Furthermore, monoaxial orientation of both neat and blended COC resins can form shrink films with high shrink ratios and low shrink forces.

COCs are suitable for direct food contact applications. For instance, the FDA has issued a regulation for ethylene-norbornene copolymers in dry-food-contact 1c21 CFR177.1520). COCs also comply fully with the federal Food, Drug and Cosmetic Act and all applicable food additive regulations for aqueous, acidic, fatty, and low- and high-alcohol foods. In addition, an FDA Food Contact Substance Notification (FCN 000075), which became effective August 22, 2000, provides for direct contact as films and sheets, with all food types under all conditions. COCs are also approved for many food-contact applications in Europe, where the monomers in their manufacture are listed in applicable European Union directives.

Processing

COCs are processible by all conventional methods, including injection molding, cast and blown film extrusion and coextrusion, injection blow-molding, and injection-stretch blow molding. They do not need drying or other pretreatment before molding.

For injection molding, COCs have good flowability, easily reproduce submicron-size surface features, and fill complex thin-walled parts. They also have low and substantially isotropic shrinkage during molding, resulting in little warpage. Molders can add up to 10% regrind. Cycle time typically varies from less than 10 seconds to one to two minutes, depending on the part and application.

In post-molding operations, COCs are readily metallized by vacuum deposition with aluminum, chromium, silver, or other metals. COC parts can be bonded with polyurethane adhesives, or solvent-bonded with cyclohexane or heptane. Because COC surfaces are highly inert, they should be modified before coating, for example, by corona or plasma treatment. In machining COC parts by drilling, turning, or other means, water should be the lubricant, not oil. Also, relatively slow speeds and shallow cuts should be used to avoid cracking the part. ■

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