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Cyclic Olefin Copolymers

INTRODUCTION

High transparency polymers have been available for many years as replacements for conventional glass applications, such as optical lenses. They include polycarbonate (PC) and polymethyl methacrylate (PMMA). Polycarbonate has good mechanical and thermal properties, such as anti-heat aging and impact strength. However, polycarbonate has poor resistance to organic solvents. Polymethyl methacrylate also has poor chemical resistance to organic solvents, such as ethyl acetate, toluene, and acetone.

Development of polymers having well balanced properties such as high transparency, high heat resistance, good anti-heat aging, good chemical resistance, low moisture absorption, low double refraction (birefringence), and superior mechanical strength is a goal of polymer producers. A balance of these properties in a reasonable cost material would be an opportunity for commercial success.

A family of products that has been developed that satisfies these requirements is the cyclic olefin copolymers (COC), also called cyclic olefin polymers (COP). Cyclic olefin copolymers are based on comonomers such as ethylene and norbornene, and are designated as cyclic due to the presence of the ring-like structures in the side chain on the backbone. Although cyclic olefin copolymers are amorphous, the structure of the cyclic olefin comonomer is rigid, and hence, the copolymers are rigid. Other properties of cyclic olefin copolymers are a combination of those of polyolefins and amorphous polymers. For example, physical properties such as chemical resistance and wear strength are more similar to polyolefins, while properties such as mechanical strength and flow are more similar to amorphous polymers.

CURRENT TECHNOLOGY

There are two main categories of cyclic olefin copolymers:

- Ring-opening metathesis polymerization (ROMP) products – these resins are most often either thermosets used for reaction injection molding (RIM) or thermoplastics based on a molecular weight controlling hydrogenation step. Both RIM and thermoplastic copolymers include rigid and elastomeric materials; typical cyclic olefin ROMP polymers and copolymers include Telene® DCPD resins from Telene (formerly BF Goodrich) and the semi-crystalline rubber VESTENAMER® by Evonik (formerly Degussa and Huls). ROMP products that do not result in amorphous transparent resins are not covered in this report, as these resins do not contain a cyclic structure along the polymer chain. Two exceptions are JSR’s ARTON and Zeon’s ZEONEX and ZEONOR, which are made via ring-opening metathesis, but which maintain a cyclic structure in the backbone of the polymer because the monomer used is bicyclic or tricyclic.

- Non-ring-opened products – the polymer chain of these resins forms from an olefin polymerization reaction, similar to conventional polyolefins, with no ring opening, in the presence of a catalyst. These are amorphous transparent materials, with low moisture absorption, good chemical resistance, and good mechanical strength. These resins are the
focus of this report. Mitsui Chemical’s APEL and TOPAS Advanced Polymers’ TOPAS are included in this category.

A schematic showing the two polymerization routes is shown in the figure below.

Typical Polymerization Routes for Cyclic Olefin Copolymer

In this report, although most references are made to cyclic olefin copolymers, this is also meant to include cyclic olefin polymers, unless specifically stated otherwise.

- Comonomer Selection and Production

The selection of the cyclic olefin is made so that polymer properties are optimized and production cost is kept to a minimum. The monomers of choice have been norbornene (NB) and tetracyclododecene (TCD) or derivatives of them. Comonomer selection and production is discussed in this report.

- Cyclic Olefin Copolymer Production

The major cyclic olefin copolymer and polymer processes are reviewed in this section. The main differences in production relate to comonomer used, catalyst used, and whether the main reaction is chain polymerization or ring-opening metathesis with hydrogenation.

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PATENT REVIEW

A patent review of work being conducted by the principal companies involved in cyclic olefin copolymer production technology is included.

- JSR Corporation currently produces six different grades of ARTON. These grades are targeted at three main applications – plastic lenses (e.g., camera lens for mobile phones, objective and sensor lens for mobile phones), light guiding plates (or panels), and optical film. JSR also produces ARTON optical film for LCD retardation films and touch panels.

- Mitsui currently produces seven grades of APEL. Five of the grades are available for general purpose applications (sheet, film, bottle, industrial parts, medical packaging), while two grades are for optical and injection molding applications.

- TOPAS Advanced Polymers currently markets seven basic grades of TOPAS COC resins, which are made for injection molding and extrusion applications. TOPAS COC resins are targeted at four main applications: healthcare (medical, pharmaceutical, diagnostics), packaging (films, sheet, labels, shrink wrap), electronics (antennas, printed circuit boards, insulators), and optical (lenses, light guides, films, sensors). Smaller applications include toner binder for color printers and the emerging markets of compounds, foams, and fibers.

- Zeon currently produces ten grades of ZEONEX and four grades of ZEONOR. The high-grade ZEONEX is mainly used for optical devices such as lenses and prisms for mobile phone cameras, digital cameras, and compact cameras, as well as lenses for electronic office equipment, pick-up lenses for CDs and DVDs, and containers and packaging material for medical products. Standard-grade ZEONOR is mainly used for general purpose transparent engineering plastic applications, such as light guide plates for PCs and mobile phones, diffusion plates and optical films for LCD televisions, and optical discs, as well as, automotive lamp components and food containers.

PROPERTY COMPARISON WITH COMPETING MATERIALS

COCs were introduced into the market for a variety of applications that were focused primarily on their optical and insulative properties. In this section, a discussion of the characteristics of COCs as they apply to physical/mechanical properties, processability, and performance, and how they compare to the materials they compete with is given.

ECONOMICS

Costs of production estimates are presented for cyclic olefin copolymers and the materials they compete with. Specifically, cost estimates for the following processes have been evaluated:

- Production of Norbornene
- Production of Tetracyclododecene
- Production of Cyclic Olefin Copolymer from Norbornene with Metalloocene Catalyst.
- Production of Cyclic Olefin Copolymer from Tetracyclododecene with Ziegler-Natta Catalyst
- Production of Polycarbonate via interfacial polymerization process
• Production of Polymethyl Methacrylate (PMMA) via continuous bulk process

In all cases, costs of production estimates have been given for Japan and Western Europe, the two locations where COCs are currently produced.

All cost tables given in this report include a breakdown of the cost of production in terms of raw materials, utilities direct and allocated fixed costs, by unit consumption and per metric ton and annually, as well as contribution of depreciation to arrive at a cost estimate (a simple nominal return on capital is also included).

COMMERCIAL APPLICATIONS & REGIONAL MARKET REVIEW

Based on performance characteristics, cyclic olefin copolymers (COC) materials compete in some markets targeted by polycarbonate (PC) and polymethyl methacrylate (PMMA) in certain niche areas where they can offer a performance-related advantage. Therefore regional demand for PC and PMMA is summarized in the report (North America, Europe, Japan/China, Rest of the World).

Global market size and capacities for cyclic olefin copolymers have been estimated in the report.
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