

**P A R A L L E L**

# **MATERIAL SELECTION**

for microfluidic devices

# Introduction

One of the most critical considerations in the design of microfluidic devices is material selection. The composition of a microfluidic chip often drives the functionality of the device; material properties can influence optical behavior, surface chemistry, reagent compatibility, temperature resistance, and many other characteristics. Further, the chosen material can impact the cost, reliability, and scalability of a microfluidic system. The following insights into commonly used polymers for microfluidics are presented to help inform the material selection process early in the design process and ensure the functionality of a given chip design.

## Background of materials used in microfluidics

To understand the benefits and trade-offs of different polymers used in microfluidic systems it is important to first understand the history of different materials employed in the field. These different materials are used for a variety of reasons ranging from performance advantages to ease of manufacture.

### Silicon and glass

The earliest microfluidic chips were inspired by the microelectronics industry and as such relied on wafer fabrication processes. These types of chips are typically made of etched silicon and glass that is anodic bonded in a microfabrication facility. The main advantage of making chips in this way is that extremely small and intricate features can be produced and integrated into complex assemblies with sensors and other electronic components. Additionally, silicon and glass exhibit a surface saturated with negative charge; these negative charges can be used to promote wetting or can even be used to pump fluid through the device using

electro-osmotic flow. Despite these advantages, the manufacturing process is slow and requires a dedicated microfabrication facility with expensive equipment and hazardous chemicals. This makes silicon and glass chips more costly than other alternatives and are therefore only used in systems with reusable chips or in the most demanding of applications.

### Polydimethylsiloxane (PDMS)

Due to the complexity and cost of manufacturing silicon and glass components, researchers needed an alternative material for manufacturing microfluidic prototypes. In 1998, researchers at Harvard University led by Dr. George M. Whitesides discovered that microfeatures could easily be replicated from a master mold using polydimethylsiloxane, or PDMS. PDMS is a high purity silicone used in a wide range of applications including food products, cosmetics, lubricants, medical devices, and is a primary ingredient in Silly Putty. PDMS exhibits many advantages for replication of microfluidic devices in a lab. First, it is a high purity polymer that is relatively inert, optically clear, biocompatible, and gas permeable making it suitable for many cell culture, analytical, and imaging applications. Second, PDMS can be covalently bonded to glass by means of plasma induced oxidation making it easy to produce a sealed device. Lastly, molds for PDMS devices can be made using a variety of methods including 3D printing, CNC machining, and direct write lithography.

Although PDMS can be readily produced in a lab, it is much harder to produce at scale. Due to the casting process, PDMS is not suitable for medium to high volume production and is subject to many quality control issues including part to part variability and inconsistent material properties. Furthermore, some of the properties of PDMS make it disadvantageous for microfluidic applications. The polymer has limited

solvent resistance, typically manifesting in swelling of the polymer matrix rather than degradation of the polymer chains. PDMS is also subject to dimensional instability due to a low durometer, likelihood of swelling, and a high coefficient of thermal expansion. Finally, PDMS is known to adsorb and absorb small molecules such as hormones and drugs, an issue that will be discussed in detail later in this whitepaper.

## **Thermoplastics**

Thermoplastics are a class of polymer that are melt processable and suitable for manufacturing processes such as extrusion, thermoforming, and injection molding. This property tends to make them more affordable and suitable for high scale manufacturing. Thermoplastics are generally divided into two categories: semi-crystalline and amorphous polymers. The structural differences in these polymer networks lead to major differences in their properties which will be discussed below.

### **Semi-crystalline polymers**

A semi-crystalline polymer is a polymer with some degree of organized structure, often as a result of cross linking between polymer chains. The ordered microstructure of the polymer network improves the chemical and thermal resistance of the polymer and also tends to increase its strength and stiffness. While these properties make semi-crystalline plastics better performers in many technical applications, they also make them more difficult to process; semi-crystalline plastics require higher processing temperatures and tend to be harder to extrude or mold than amorphous alternatives. In addition to the processing cost, the types of monomers and polymerization reactions required tend to make the bulk material more expensive. In the field of microfluidics, these polymers tend to be used for larger components such as pneumatic manifolds and fluid sample

loops where chemical resistance and long term reliability are required but microfeatures are not present. In some cases, semi-crystalline polymers are used for supplemental elements such as membranes, vents, and diaphragms. Some examples of semi-crystalline polymers include polyether ether ketone (PEEK), polyetherimide (PEI), polyimide (PI), polytetrafluoroethylene (PTFE), and polysulfone (PSU).

### **Amorphous polymers**

Any plastic with irregularly oriented polymer chains is generally classified as an amorphous polymer. In an amorphous polymer, the polymer chains are closely packed together and intermolecular forces hold the polymer together. Due to this randomized structure, amorphous polymers tend to be lower stiffness, softer, and less temperature resistant than semi-crystalline materials. Many amorphous polymers also display better optical properties, are more isotropic, have lower shrinkage rates, and reproduce small features better than semi-crystalline materials.

Although amorphous polymers do not have a crystal structure, they can still have some degree of organized structure. For example, extruded amorphous plastics may still have internal stresses present in the polymer network and may become stronger in the direction of extrusion. Unlike semi-crystalline polymers, amorphous polymers tend to have lower solvent resistance and no defined melting point. Instead, these polymers gradually soften at elevated temperatures. The point at which the elastic modulus decreases significantly and the polymer interactions increase is typically denoted as the glass transition temperature. At this temperature the polymer chains are able to move around and reorganize; this behavior is what allows amorphous thermoplastics to be thermally bonded and sealed. The main amorphous

thermoplastics used in microfluidics are polystyrene (PS), poly-methyl-methacrylate (PMMA), polycarbonate (PC), cyclic olefin copolymer (COC), and cyclic olefin polymer (COP).

### **Thermoplastic elastomers**

A subset of thermoplastic polymers containing both crystalline and amorphous properties are called thermoplastic elastomers, or TPEs. TPEs are highly elastic thermoplastics that have properties similar to rubber or silicone but with the processing advantages of other thermoplastics. They are often used to create seals, membranes, adhesives, and other components and are common in microfluidic systems. TPEs are typically a combination or blend of two or more polymers, or a block copolymer of rigid and elastic monomers. They usually contain some degree of cross linking and most are lower temperature materials. Many categories of TPEs exist such as polyurethanes (PU), styrenic block copolymers (SBC, SBS, SEBS), copolyester elastomers (COPE), and polyolefin elastomers (EVA, EPDM). For a given thermoplastic, there usually exists a thermoplastic elastomer with similar properties that is chemically compatible and able to be joined in a secondary process or used as an interface between two dissimilar polymers.

### **Copolymers**

Many thermoplastics are a blend or compounded polymer of two or more species. Copolymers may be used for cost reduction or for performance enhancement; typically a copolymer expresses the advantages and disadvantages of its constituent species. For example, styrene methyl methacrylate (SMMA), has similar optical and mechanical properties to PMMA with the added solvent resistance of PS. More importantly, the use of a copolymer allows for more adjustment of material properties and for a wider range of material

grades. This will be discussed later when comparing the differences between COC and COP.

### **Optical polymers for molded microfluidic applications**

With few exceptions, the most common amorphous polymers used in the mass production of microfluidic devices are PS, PMMA, PC, COC, and COP. Specific advantages of these materials and differences in their properties will be discussed below, followed by a section highlighting key properties that are aimed to inform the material selection process.

### **The transition molding process**

At Parallel Fluidics we produce devices using a proprietary process called transition molding. This process produces similar results as injection molding, but is much faster and suitable for smaller quantities at a lower cost. We have selected specific grades of injection molding materials and optimized them for this process. One material that is missing from the list is polystyrene, which has poor thermal properties that make it better suited for monolithic components such as plates, inserts, and other consumable labware. Commercial microfluidic devices that use polystyrene are usually lower value goods such as paper based assays and adhesively laminated diagnostic chips.

### **Poly-methyl-methacrylate (PMMA)**

PMMA is a general purpose optical polymer that is suitable for a wide range of microfluidic applications. One of the main advantages of PMMA is that it is slightly more hydrophilic than other amorphous thermoplastics making it easier to wet microfluidic channels. Grades without an impact modifier have excellent optical properties down to 340nm with relatively low dispersion characteristics. The main disadvantage of PMMA is solvent

resistance; PMMA tends to craze when exposed to alcohols and dissolves in most organic solvents. PMMA serves as a great material for microfluidic prototypes (especially as an alternative to polystyrene), droplet generators, imaging applications, and low temperature devices. The production cost of PMMA devices is lower than other materials due to the material cost, processing temperatures, and excellent bonding characteristics. Here at Parallel Fluidics we offer a styrene modified grade that has improved alcohol resistance, no impact modifier, and great molding characteristics.

### **Polycarbonate [PC]**

Our most flexible, durable, and temperature resistant material, PC has long been used in microfluidic applications requiring high temperatures or thermal cycling. Typically this material is used for applications involving polymerization reactions such as PCR or hydrogel droplet production but may be suitable for other applications as well. Despite being relatively high performance considering its low cost, polycarbonate has a few disadvantages for sensitive applications. Optically, PC is best in the visible spectrum and achieves good results for bright-field microscopy, but suffers from high dispersion, high index, birefringence, and autofluorescence.

### **Cyclic olefin copolymer [COC]**

A copolymer of ethylene and norbornene, COC serves as a suitable material for most microfluidic applications. COC is resistant to most organic solvents and can be used for pharmaceutical, diagnostic, analytical, and other applications. A variety of grades exist with a wide range of mechanical and thermal properties. The surface of COC is nonpolar and hydrophobic, making it particularly useful for droplet applications that use fluorinated oils as a continuous phase. Most COC grades are relatively temperature resistant and stable up to 105C.

COC also has great optical properties including high UV transmission, low birefringence, and a similar index of refraction to water. Additionally, COC has very low rates of vapor permeability and water absorption. The main downside to COC is that the raw material cost is slightly higher than PMMA and PC and that the processing of COC parts and extruded materials is more difficult.

### **Cyclic olefin polymer [COP]**

COP is chemically similar to COC and can often be used interchangeably. The material has similar solvent resistance, optical properties, and temperature resistance. Generally, COP is a more stable polymer that remains nonpolar over time and exposure to other compounds and treatments. This leads COP to be a great material for packaging of biologic drugs and pharmaceutical devices. The stable surface chemistry gives it a slight edge over other materials for reducing adsorption and improving compound recovery. That said, these properties also negatively impact the bonding characteristics and adhesive compatibility of COP when compared to COC.

### **Other considerations**

A few other considerations should be made when deciding which material to use. A few of the major factors to think about when choosing a material are listed below.

#### **Gas permeability**

All of the thermoplastics offered at Parallel Fluidics exhibit much lower gas permeability than that of PDMS. Reduced gas transfer into and out of the device might impact device performance when compared to a PDMS chip. This may result in reduced oxygen levels for cell culture applications, lower availability of atmospheric gasses for chemical and metabolic reactions, and the potential for gasses to remain trapped

inside of the chip due to a change in solubility. Many of these issues can be addressed in the device design by using gas permeable tubing, a bubble trap, or additional means of gas transfer.

### Surface adsorption and molecule absorption

Special care should be taken to evaluate surface adsorption (molecules binding to the surfaces of a device) and volumetric absorption (molecules dissolving into the bulk material of a device). Glass and silicon devices may experience high levels of surface adsorption due to their negatively charged surface and PDMS devices are known to absorb small molecules into the bulk polymer matrix. This often results in unexpected changes of chemical concentrations and issues with compound recovery. All of the thermoplastics offered at Parallel Fluidics are a major improvement in this regard, offering lower degrees of surface adsorption and are unlikely to absorb most drugs, hormones, and other small molecules. The best material in this regard is COP, which offers the best solvent resistance and highest compound recovery of all optically transparent amorphous polymers.

### Impact modifiers

Largely found in PMMA materials, impact modifiers are typically elastomeric additives that increase the flexibility and impact strength of a polymer matrix. Many impact modifiers are a butadiene-based MBS or SBS polymer and may require the use of a UV stabilizer. For this reason, impact modified materials tend to have lower UV transmission and may exhibit fluorescence at some wavelengths. The addition of an impact modifier is often beneficial in extruded materials to improve handling and secondary processing. The PMMA material used for the fluidic layer at Parallel Fluidics is free of impact modifiers, but the cap material contains an impact modifier to improve manufacturability of capped devices.

### Solvent resistance

For most applications, devices made of COC or COP will exhibit the widest solvent resistance. In particular, they are safe with most organic solvents, acids and bases, and polar compounds. When handling highly volatile and aggressive reagents, it is advisable to do a thorough investigation of solubility parameters and material testing.

Solvent	PMMA	PC	COC	COP
Alcohols (IPA, EtOH)	Yellow	Green	Green	Green
Acetone	Red	Red	Green	Green
Fats and Organic Oils	Green	Green	Yellow	Yellow
Acids and Bases	Yellow	Yellow	Green	Green
Polar organic solvents	Red	Red	Green	Green
DMSO	Red	Red	Green	Green
Fluorinated Oils (FC-40)	Green	Green	Green	Green
Chlorinated Solvents (i.e. DCM)	Red	Red	Red	Red

\* Chemical compatibility is application dependent and may depend on solution concentrations, residence time, and reaction kinetics.

Table 1: Solvent resistance of thermoplastics

Many solvent interactions are dependent on concentration, temperature, and individual grade of material and should be evaluated on an application by application basis.

### **Regulatory compliance**

For most microfluidic applications involving cell culture it is recommended to use materials that are USP Class VI and ISO 10993-1 certified. Most materials offered at Parallel Fluidics have been sourced to meet these requirements with detailed information available upon request.

### **COC vs COP: How to choose?**

The main difference between COC and COP is due to ethylene content. Both polymers contain ethylene, but the content and location of the ethylene chains are very different. The ethylene chains in COP are contained between repeated monomers while COC is a copolymer with long chains of ethylene attached to repeated norbornene units. These longer and exposed chains of ethylene improve the adhesive and bonding properties of COC. It also tends to accept coatings and surface treatments better than COP.

COC tends to be more stiff making it suitable for extrusion applications. Individual grades of COC are developed by increasing the molecular weight and norbornene content to make the polymer more temperature resistant at the expense of ductility and cost. Conversely, compounds with a very high ethylene content (40-60%) tend to exhibit a degree of crystallinity that results in elastomeric properties.

The high-flow properties of COP make it great for injection molding, but more difficult to extrude. COP tends to reproduce small features better than COC, but both are excellent in this regard. Unlike COC, COP grades are largely distinguished by additives and differences in molecular weight. COP

has an advantage for higher temperature applications because the high temperature grades are more flexible than high temperature grades of COC. This makes them easier to eject from a mold, easier to handle in secondary manufacturing procedures, and less likely to be damaged when mechanically stressed. Further, the cost offset between COC and COP becomes negligible for high temperature grades as the high norbornene content in temperature resistant COC grades makes them more expensive. A disadvantage of COP is that there are fewer suppliers and medically certified grades to choose from.

It also is worth noting that the two polymers are chemically compatible and that a COP chip can be capped with a COC film. This is especially useful in high temperature applications as it allows for easier molding of the fluidic layer in combination with a lower cost and easier to bond film for the cap.

### **Cost**

At the prototyping scale, the cost of materials is negligible. For small chip quantities the cost of material is approximately the same for all of the above polymers. At production quantities the cost of PMMA and PC is lower than COC and COP, but typically the cost of material is lower than other factors in the manufacturing process. For most applications, it is generally advisable to choose the best performing material rather than save on cost.

## **Our solution**

At Parallel, we offer industry standard materials that are suitable for injection molding and scale production. An overview of key material properties are provided in the table below:

		PMMA	PC	COC	COP
Tensile Modulus	MPa	3100	2400	3200	2300
Tensile Strength	MPa	74.5	65	46	60
Elongation at Break	%	4	120	1.7	16
Impact Strength (Notched)	kJ/m2	11	14	13	13
Glass Transition Temperature	°C	105	146	134	136
Moisture Absorption	% (23°C, sat.)	0.2	0.3	0.01	0.01
Melt Flow Rate	g/10min	10	20	43	30
Index of Refraction	-	1.49	1.586	1.533	1.533
Optical Transmission	%	93	88	91.4	92

Table 2: Material properties of thermoplastics

## Design recommendations

Deciding the right material to use for a given microfluidic application can be a challenge. Sensitivities to surface characteristics, wettability, optical properties, and other behaviors can make it difficult to identify the best material for the job. To get more insight into material properties please head to our design guide and download our material datasheets to compare properties or contact us for more information. We are happy to provide material recommendations for the best chances of success.

## Design feedback

Providing feedback is a core part of our process here at Parallel. We'll check your device to make sure that it complies with best practices and suggest changes that may be necessary to ensure success of your design. Upload your design today to receive a configurable quote that will allow you to

adjust materials, configuration, quantities, and lead time on the fly.

## About Parallel Fluidics

Parallel Fluidics is a rapid manufacturer of microfluidic devices. Upload a design now to get a quote for high quality prototypes in as little as three days.

Visit our website for more design resources, embeddable components, and accessories to help accelerate the microfluidic development process.

Reach out to

[info@parallefluidics.com](mailto:info@parallefluidics.com)

to connect