

Materials for 3D Printing by Fused Deposition

Bates-Green, K.¹, and Howie, T.²

¹Institute of Flight, Mukilteo WA 98275

²Edmonds Community College, Lynnwood WA 98036

ABSTRACT

The lesson includes lecture materials and demonstrations/activities for illustrating concepts related to polymer properties in 3D printing. A basic overview of polymer structure and behavior is followed by classroom activities, and then a more in-depth discussion of the specific polymers used in common fused deposition modeling (FDM) printers. The effects of chemistry and structure on the properties of the selected polymers are discussed, especially as they relate to the use of those polymers in FDM 3D printing.

LEARNING OBJECTIVES

- Identify eight common FDM materials and their chemical structures
- Compare relevant material properties that affect printing behavior
- Relate chemical structure to material properties and the variability of properties
- Successfully perform 3 activities that illustrate comparative FDM usage

AM CORE COMPETENCIES

11Aa3: Compare the differing properties and characteristics of common materials used for additive manufacturing models

11Aa1: Fabricate a part or an assembly using additive manufacturing equipment

11Aa6: Discuss the post-processing support for the completion of rapid prototype models

MatEdU CORE COMPETENCIES

0Cc1: Demonstrate workplace safety methods

0Dd1: Recall key job-related information (processes, references, terminology, acronyms)

1Cc1: Demonstrate familiarity with safe laboratory practice

Key Words - Fused Deposition Modeling (FDM), thermoplast, pendant group / side group, crystalline, amorphous, crazing, glass transition temperature, polarity.

Type of Module - Lecture, PowerPoint, optional Demonstrations or Activities

Time to complete - One to five 50-minute classes, depending on knowledge and level of students

Target Grade Levels: Secondary and postsecondary



This work is part of a larger project funded by the Advanced Technological Education Program of the National Science Foundation,
DUE #1501251

Contents

Abstract.....	1
Learning Objectives	1
MatEdU Core Competencies.....	1
Equipment.....	4
Instructor Notes and Curriculum Overview:	4
Introduction	4
Properties of Polymers for FDM	5
Polymer Structure	7
Class Activities.....	7
ABS vs PLA Print Warping	7
Crazing and Bending	8
PLA vs ABS solvation and welding/smoothing.....	9
Commonly Used FDM Plastic Materials	10
Polylactic acid (PLA) plastic.....	11
Acrylonitrile Butadiene Styrene (ABS) plastic	12
High-Impact Polystyrene (HIPS) plastic.....	13
Thermoplastic Polyurethane (TPU) elastomer	14
Polyethylene Terephthalate (PET) plastic.....	15
Nylon	16
Polycarbonate (PC)	17
Composite Printing Filament - Plastic Matrix Fills	17
Summary of Properties.....	18
Property Definitions	19
Student Evaluation Questions	20
Instructor evaluation questions:.....	20
References	21
Bibliography	21

Equipment

- FDM printer for lab activities and creation of sample parts
- FDM printed sample parts for use in lab activities
- Raw FDM filament clippings of different materials for use in lab activities
- PPE latex gloves and eye protection for working with acetone solvent

Instructor Notes and Curriculum Overview:

This module discusses only common thermoplastic materials used in Fused Deposition Modeling 3D printing. Students may be aware of other materials used in specialty FDM-type processes, such as chocolate or molten glass, or slurries such as concrete or sugar-saturated-alcohols. Students may also be aware of completely different processes, such as UV-cured plastics, laser-sintered metal powders, powders combined with binder jets, or direct-energy-deposited particles. The methods of additive manufacturing available are extremely diverse, but in this module we will address only polymeric FDM.

This module covers some of the most relevant properties to FDM printing and the source of their variabilities between and within material categories. It may surprise students that, for example, ABS is not so much a particular material as the name of a set of chemical components. Throughout this module typical materials properties of the chemicals used in FDM are discussed, but it is important to remember that any of the thermoplastic chemicals here might also have additives such as plasticizers, hardeners, or stabilizers added to change the properties. Every time a new source of FDM material is used, the manufacturer's own specifications should be considered and compared to the expected properties presented here.

Introduction

Fused deposition modeling (FDM) 3D printers create objects by extruding a material which then solidifies and is capable of having more extruded material attached to it. If such a system is computer controlled, then it is considered an FDM 3D Printer. Conceptually, any material which can flow and then harden can be used to create objects by FDM. This includes a wide range of materials from thermoplastic polymers to concrete slurry, cake icing to lab-grown human collagen. This is a rapidly changing field, but current FDM 3D printing is almost entirely focused on extrusion of thermoplastics and thermoplast-fills. Though it is not noted for each separate material in this module, it's important to keep in mind that plastics absorb a certain amount of atmospheric moisture, which can flash into steam during plastic melting and cause inconsistent behavior and jamming of the FDM extruder. This means that it is important to keep all printing filament dry in either a dehumidified space or a desiccator cabinet.

In general polymers can be split into two categories: thermoplastics and thermosets.

Thermoplastics are polymers that, after forming, can be melted and formed again (e.g polyethylene). Thermosets are polymers that once formed cannot be melted and reformed (e.g.

epoxy). Since thermosets degrade instead of melting when heated, they cannot be used in FDM and will not be discussed here.

Properties of Polymers for FDM

When choosing a thermoplastic polymer to use in a FDM, there are many properties of polymers that can contribute to how well the part prints and the resulting properties of the printed parts. The properties of interest for how well a polymer prints include melting temperature (T_m), glass transition temperature (T_g), and the coefficient of thermal expansion (CTE). The melting temperature will affect the temperature the extruder needs to be at to print the polymer. T_g along with the CTE relate to how much thermal stress is developed during printing which can affect bed adhesion. Solvent resistance, strength, and ductility are also important properties. All these properties are a function of the polymer chemistry and microstructure of the polymer. The strength and ductility of the printed part are also directly affected by the chemistry and microstructure as well. A general overview of the chemistry and microstructure are presented to understand the differences between polymers used as FDM filaments.

Polymers are made up of monomers, chemical units that can be repeated hundreds to thousands of times to create large molecular chains, which are sometimes referred to as macromolecules. The base chemical unit is called a repeat unit and the number of repeat units in a chain is known as the degree of polymerization. Examples of repeat units are shown in Figure 1.

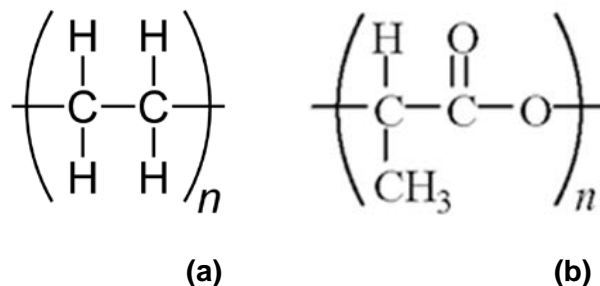


Figure 1: Repeat units for (a) polyethylene (PE) (b) Polylactic Acid (PLA)

T_m and T_g are directly related to how easily polymer chains can slide past each other at the molecular level. T_g is the temperature for each plastic at which it isn't yet melted, but at which it becomes easier for polymer chains to move, resulting in a large change in properties. Above T_g the plastic is flexible and ductile, and below T_g the polymer is more stiff and brittle like glass. In terms of chemistry the factors that can affect these properties are the chemistry of the repeat unit backbone, pendant groups, and the polarity of the bonds. Pendant groups refer to chemical groups that hang off the main carbon backbone in a polymer like the CH_3 group in PLA shown in Figure 1. Large pendant groups make it easy for polymer chains to entangle which restricts motion of the chains polymer more raising T_g and T_m . It also tends to make polymers stronger and more rigid, but more brittle [1]

Polymers with no aromatic rings in backbone (aliphatic) tend to be more flexible and have a high elongation before fracture. Aromatic rings in the polymer backbone tend to increase the strength, stiffness, and Tg of the polymer, but reduces the amount of elongation before fracture. Aromatic rings also improve flammability properties of a polymer, but are susceptible to degradation from ultraviolet (UV) radiation. Figure 2 shows the repeat units for two similar polymers with different backbone structures [1].

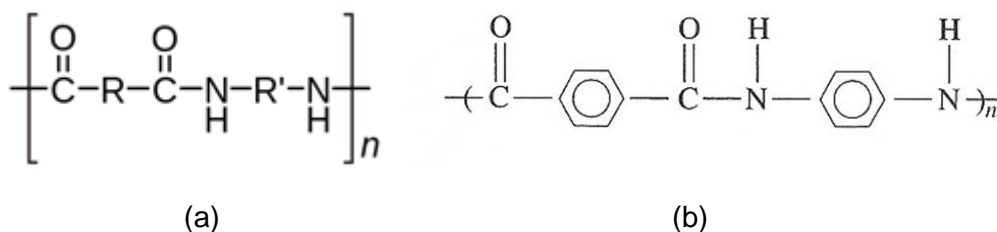


Figure 2: Repeat units for (a) Nylon (aliphatic) (b) Kevlar[®] (aromatic)

Polar bonds affect polymers in several ways. The more polar bonds that are present in the repeat unit the more likely a polymer is to absorb water, which can detrimentally affect the FDM process as well as potentially soften or degrade the material. Polar groups influence the resistance of a polymer to solvents as well. Polymers with more polar groups are more likely to dissolve in polar solvents (like dissolves like). In FDM, one way of creating a removable support structure is printing a material that is soluble in a solvent that doesn't affect the material of the part. Polar groups also have the potential to participate in dipole or hydrogen bonding, a strong form of secondary bonding method that can increase strength of the polymer through crystallization.

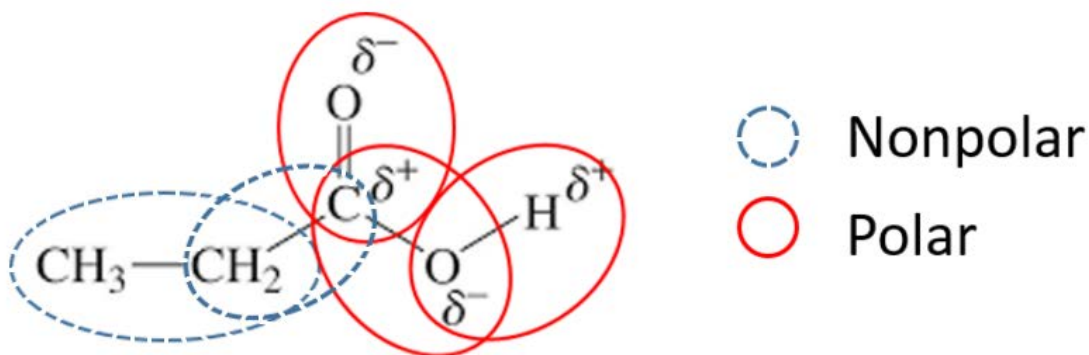


Figure 3: Organic molecule exhibiting polar and nonpolar bonds

Activity: See PLA vs ABS solvation and welding/smoothing at end of module

Polymer Structure

Thermoplastic polymers can exhibit two types of microstructures, amorphous and crystalline. Amorphous structures have no identifiable order to the arrangement of the polymer chains, similar to a pile of spaghetti noodles. Semi-crystalline regions occur when the polymer chains align and pack tightly together. Polymers will often exhibit a combination of amorphous and crystalline regions. The amorphous/crystalline structure is controlled by many factors such as repeat unit chemistry, molecular weight, processing parameters, and loading (see crazing activity). Anything that makes it harder for the chains to stack closely together such as pendant groups or stiff chains tend to cause the polymer to exhibit more amorphous structures [2].

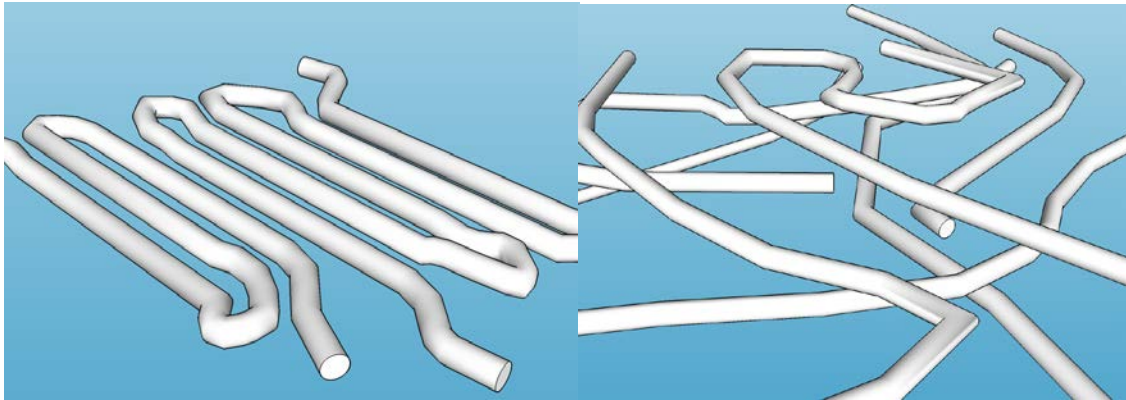


Figure 4: Polymer Microstructures - Crystalline (left), and Amorphous (right)

In terms of properties, amorphous regions tend to be more mobile and flexible and give the polymer increased ability to elongate. Crystalline regions impart greater strength, stiffness, density, and solvent resistance to a polymer, but lower its maximum elongation and optical transparency.

Also see: Crazing and Bending demonstration

Class Activities

ABS vs PLA Print Warping

Materials:

- FDM 3D printer in a well-ventilated space
- ABS (acrylonitrile butadiene styrene) filament (~6g per test)
- PLA (poly-lactic acid) filament (~6g per test)
- Printable geometry file (See attached STL file)

- Computer with appropriate slicer software to generate commands for your specific 3D printer

The FDM plastics ABS and PLA have significantly differing print behaviors, resulting from their differing properties. In this activity, you will observe these different properties during printing.

Load the file “Print Warping Sample.stl” into your slicer software, or quickly draft a rectangular or triangular solid fitting within the dimensions 40x20x2mm for printing. Generate two print files with an extruder temperature of ~215C and no build plate heat (or a room-temperature setting), one print file with a software-generated raft and another without (your slicer most likely has a “raft” option). Use standard settings, and save time printing this simple part by using a low resolution and low infill percentage.

On a clean print bed with no special adhesives, run each of your print files once each in PLA, and then again once each in ABS. Observe and/or record them as they print. If a print completely detaches from the build plate, end the print early. Otherwise, allow it to complete.

What did you observe? What were the differences between the PLA and ABS? What properties differ between the two plastics that may cause differing behavior in this case?

The expected behavior in this experiment is that both samples printed without rafts will warp somewhat during printing, with one or more corners of the printed shape pulling off of the build plate and curling up and in. This behavior should be much more pronounced in the ABS than in the PLA. Look at the Properties of FDM Materials table in this module and consider which are relevant.

The objects we printed were relatively warm for PLA, and relatively cool for ABS extrusion. More importantly, the glass transition temperature for ABS is much higher than for PLA, meaning that ABS starts to stiffen greatly at 110C, and PLA only does this at 65C. While cooling, the materials stretch while shrinking slightly until they stiffen at their T_g, and then the remaining shrinkage caused by cooling is resisted by the stiffness of the material. This means that these stresses are stored internally, bending and warping the material instead of being relieved by the warmer material’s ability to flow. Since this stiffening happens at a much higher temperature for ABS than for PLA, much more warping occurs for the ABS. Without a heated build plate, the bottom layers cool and start to shrink first, while also stiffening early in their shrinking. The difference in shrinkage rates causes warping, and stiffening at an earlier temperature during cooling exaggerated the effect.

Crazing and Bending

Materials:

- 3cm lengths of equal-diameter ABS and PLA filament
- Optional additional short filament samples

Plastics exhibit a behavior called “crazing”, a visible response to deformation when many small cracks form on the surface and scatter light. This behavior can be seen when a plastic filament is bent sharply. Obtain samples of ABS, PLA, or other FDM plastic filament, bend them 180 degrees (fully doubled over on themselves), and see what happens. Compare this behavior for multiple samples of the same plastic. Are the results consistent? In what materials is it more noticeable?

After characterizing what you have seen, think about the chemistry, especially the side groups, of the polymer chains you are experimenting with. Crazing is seen when the plastic develops microcracks as a result of stiffening while being bent. If the plastic stretches sufficiently, then cracks don’t form and crazing does not occur. This means that plastics which stiffen when bent will craze. In plastics, this stiffening occurs when amorphous regions of the plastic are forced to crystallize because of the stress being placed on them. The crystallization itself may cause the cloudiness seen in crazing as well if the crystalline regions are able to scatter light. Look at the side groups, both by size and by polarity, in the plastics you’ve bent, and consider which would be easy to push together to crystallize, and which would be difficult.

In the case of PLA, crystallization is fairly easy and is already present to a high degree at room temperature. This means that local crystallization happens under stress, and can be seen, but is not a very large effect. In the case of ABS many formulations are different, but most crystallize locally, stiffen, and crack rapidly. As a result, the effect is much more noticeable in ABS than in PLA. This is a very complex behavior in polymers, but in general you can expect that regular and polar structures will make crystals more easily, and irregular structures, large side groups, and branches will resist crystallization.

PLA vs ABS solvation and welding/smoothing

Materials:

- Acetone solvent
- Non-polymer brushes
- Lab glasses and latex or nitrile gloves
- ABS filament (~3g per test)
- Geometry to print (or see attached STL file)
- Paper towel or chemical-resistance surface

As discussed in the section on ABS, this polymer can be strongly attacked by some commonly used solvents like acetone, benzene, and petrochemicals. While this is a weakness, this behaviour can also be exploited to manipulate ABS parts in post-processing.

Print two of the attached file “Lincoln.stl”[3], or any other small object desired, with standard settings in ABS. After doing so, use a brush and a small amount of acetone to paint one half of a sample with acetone. Observe the effect the solvent has on the surface. Adding too much solvent to a thin or porous surface will trap acetone vapor inside the printed object, resulting in gradual softening of the entire shape and requiring a very long time to off-gas and re-stiffen. Attempt to smooth the curved surfaces of the print into a true curve by painting and drying the solvent, and see what results are obtained. The direction of your brush strokes will also have an effect.

After observing what solvation does to the surface finish, try “plastic welding” your two samples together by painting flat surfaces with the acetone and quickly pressing them together gently, and twisting the surfaces into place to cause the solvated chains to mix together as well as possible.

The experiments suggested here will have somewhat different results depending on the grade of ABS used, the ambient temperature, the concentration of the acetone used, and even the humidity that the printed parts have been exposed to. Looking at the size of an acetone molecule and the polarities it will have, why would it be so easy for acetone to attack ABS polymer?

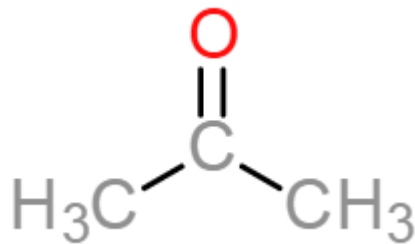


Figure 5: Acetone molecule

Acetone is a small molecule with an electronegative oxygen protruding. The oxygen will have a partial negative charge, and the central carbon will carry the positive charge inside the molecule where it is partially protected. The methyl groups are highly nonpolar. Looking at the section on ABS, note that it has large regions of nonpolarity interrupted by C-N bonds where the nitrogen will take some negative charge from the carbon. Unlike polar solvents like water, acetone will stick well enough to get between chains of ABS. Once there, acetone molecules can form pockets that separate chains from each other and allow the plastic to flow like a thick fluid, until the acetone dissolves.

Commonly Used FDM Plastic Materials

To be used for FDM printing, a material must be able to flow into place in a controlled manner and then solidify. Thermoplastics are ideal for this application. A variety of final properties may be desirable, such as different stiffnesses and elasticities, but there are some properties for FDM that have optimal ranges for production purposes. Having a low coefficient of thermal

expansion will help reduce internal stresses caused during cooling, and keep the final part dimensionally closer to the original 3D model. A low glass transition temperature will mean the part softens faster when heated, but will also reduce any warping caused during printing since the part will finish cooling more before stiffening. Strong secondary bonding will help the final part have better layer-to-layer adhesion. A lower melting temperature makes a material easier to print with, but the parts made will have more limited uses. Below, we will discuss some of the plastics commonly used for FDM, and call out properties that are especially important to their performance.

Poly(lactic acid (PLA) plastic

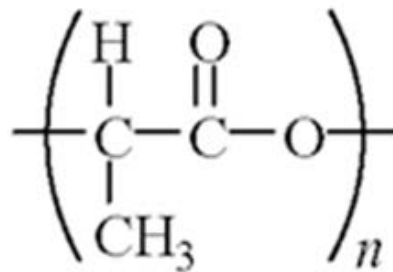


Figure 6: PLA repeat unit

Poly(lactic acid), one of the most common FDM materials, is best known as a biodegradable polymer produced from renewable sources like corn starch. Since lactic acid is naturally produced and removed by the human body, some grades of PLA are used for medical implants that are intended to harmlessly break down over time and be replaced by growing tissue. The chemical monomer produced by most natural fermentation is the levorotary enantiomer, and polymerizes to the bioactive Poly-L-lactic acid (PLLA). Lactic acid production by chemical synthesis produces equal parts of the dextrorotary and levorotary enantiomers, so Poly-DL-lactic acid (PDLLA) made from both monomers is also available, and is less biodegradable and not approved for use in medical implants. Like most polymers, one name covers a variety of different products with differing behaviors. The greatest advantages for PLA in FDM printing after its biodegradability are the fact that it creates no toxic gases while melting and so can be printed with no ventilation system, and its low glass transition temperature. Most PLA formulations soften at the glass transition temperature of 60-65 °C, where the material suddenly loses its stiffness but does not yet change phases. This can be a problem in parts that need to remain stiff in heated environments, but it also means that extruded PLA has more time to relax any internal stresses as it cools. This means that PLA parts can often be printed in unheated atmosphere with no build plate heat and no special adhesives without warping, due to the reduced stresses it retains from cooling shrinkage. However, PLA is generally not considered to be a good structural material due to its low impact strength and temperature stability compared to other FDM plastics. PLA melts around 175 °C, but flows and is extruded around 215 °C.

PLA has an aliphatic backbone with and polar carbon-oxygen bonds, which allows it to form a semi-crystalline structure. The crystalline structure and methyl (CH₃) pendant group imparts strength to polymer, but also makes it brittle. The polar bonds in PLA can make it susceptible to water absorption which can cause issues because water can partially breakdown PLA causing it to become even more brittle.

Acrylonitrile Butadiene Styrene (ABS) plastic

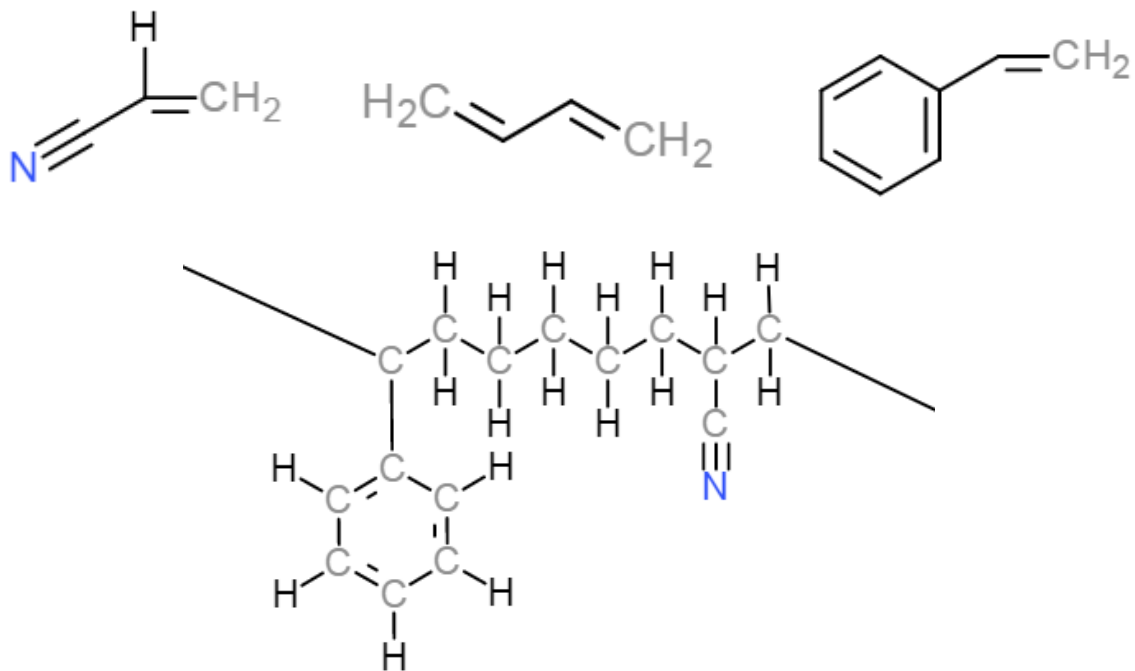


Figure 7: Monomers of Acrylonitrile, Butadiene, and Styrene (left to right at top), and one possible arrangement of these monomers combined as ABS (bottom)

Acrylonitrile Butadiene Styrene is a common 3D-printing filament material. Different grades of the plastic exist, as with all plastics, due to having different degrees of polymerization, and crystallinity, variation in chain length distribution, and added plasticizers and dyes. ABS is particularly variable due to the fact that the three monomers used in its production can be added in different ratios and at different stages, resulting in both blends and copolymers that are labeled as ABS. The form of ABS used for printing filament is very similar to that used in injection-molded parts such as Lego bricks. ABS produces toxic gases while melting, producing a notable scent and causing headaches quickly. It is always recommended to make sure any ABS FDM is done in a well-ventilated space. ABS is favored for its rheological properties which make relatively smooth surfaces in FDM. ABS plastic is not resistance to many solvents, but this can be used as an advantage when smoothing the surface of printed parts using an acetone wash or vapor. ABS's major drawback for common FDM is its high glass transition temperature, which causes it to retain internal thermal shrinkage stresses early in a print and

often warp and peel away from the build plate. Remedies for this issue include generation of rafts and supports, maintaining an elevated build plate and/or atmospheric temperature, using a ducted fan to equalize the temperature of the plastic at the point of deposition, and use of chemical adhesives on the build plate. Most ABS for FDM is extruded around 220 °C, with an elevated build plate temperature depending on the requirements of the operator. Though it is variable, most ABS softens at glass transition around 105 °C.

ABS interesting mix of properties comes from the three components. ABS has an amorphous structure due to polystyrene's large pendant group which also adds stiffness through entanglements. The rubbery butadiene imparts toughness to the material and acrylonitrile adds resistance to heat and environmental degradation.

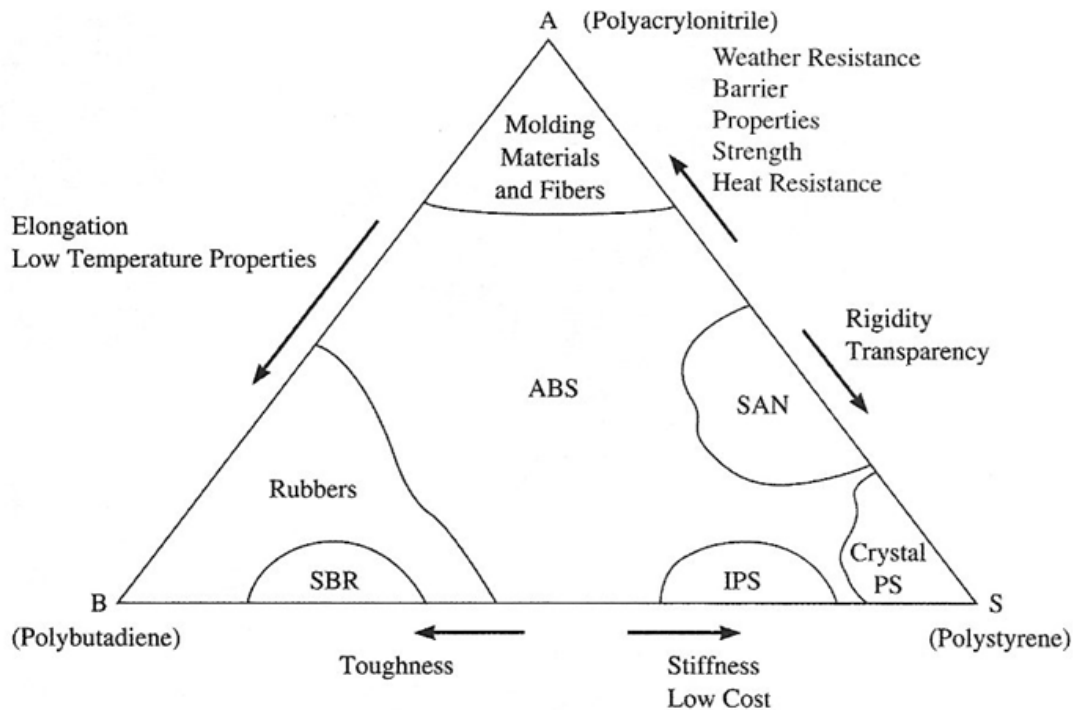


Figure 8: Properties of different mixtures of Acrylonitrile, Butadiene, and Styrene

High-Impact Polystyrene (HIPS) plastic

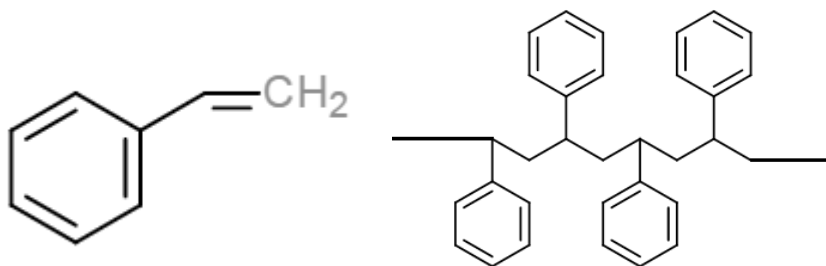


Figure 9: The Styrene monomer (left), and a section of Polystyrene chain (right)

High-Impact Polystyrene (HIPS) is suitable for FDM, but its main use is often creating rafts and support material in contact with the object being printed. This is because it can be dissolved in solvents that don't affect ABS. It is made of styrene and butadiene monomers, giving it more flexible chains for better impact resistance than simple polystyrene, and lacking the polar nitrile side-groups of ABS. Creating support structures out of a different material than the model itself in FDM is often a good strategy, because cooling after printing results in materials with different thermal expansion coefficients naturally attempting to separate. HIPS can be dissolved in a number of solvents, most notably in terpene chemicals like d-Limonene. Biodegradable solvent combinations also exist, which degrade HIPS to a form which can be diluted and handled by normal water treatment plants. HIPS is best broken down in a warm circulating solvent bath, and devices are sold for this purpose. Polystyrenes like HIPS are very rapidly dissolved by acetone. HIPS scrap is also highly recyclable, unlike polystyrene foams. HIPS is extruded around 225 °C in FDM.

In many ways the structure and properties of HIPS are similar to ABS because they share two of the same components. As noted though the solvent resistance of HIPS is different because it does not contain acrylonitrile.

Thermoplastic Polyurethane (TPU) elastomer

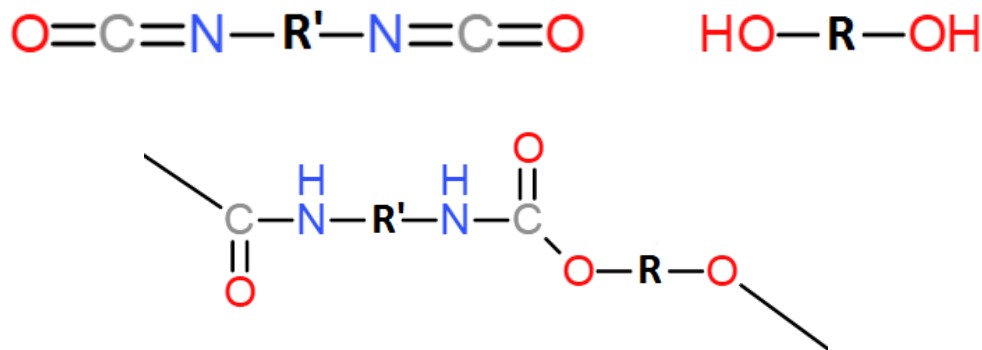


Figure 10: TPU monomers and repeat structure, where R and R' indicate regions whose chemistry varies depending on the choices of the producer

Thermoplastic Polyurethane is one example of FDM-printable flexible material. TPU is a block copolymer made of long nonpolar regions that slide past each other easily, giving it flexibility, and short polar regions that crystallize, maintaining a set structure. The result is a material that deforms and elongates easily under pressure at room temperature by shifting the nonpolar chains, but returns to its preferred shape as long as the crystalline regions stay intact. This behavior of having molecular regions that shift but remain organized by regions that don't shift is essential to creating an elastomeric, rubbery, material. In essence it creates a molecular spring. TPU in particular is commonly used because it is made in a grade which melts at easy FDM temperatures around 230 °C, and because it is resistant to abrasion and solvents like petroleum

chemicals. This means TPU can be printed into custom flexible shapes like gaskets and seals that need to resist degradation. Flexible materials for FDM other than TPU exist, usually as soft variations of other plastics discussed here.

Polyethylene Terephthalate (PET) plastic

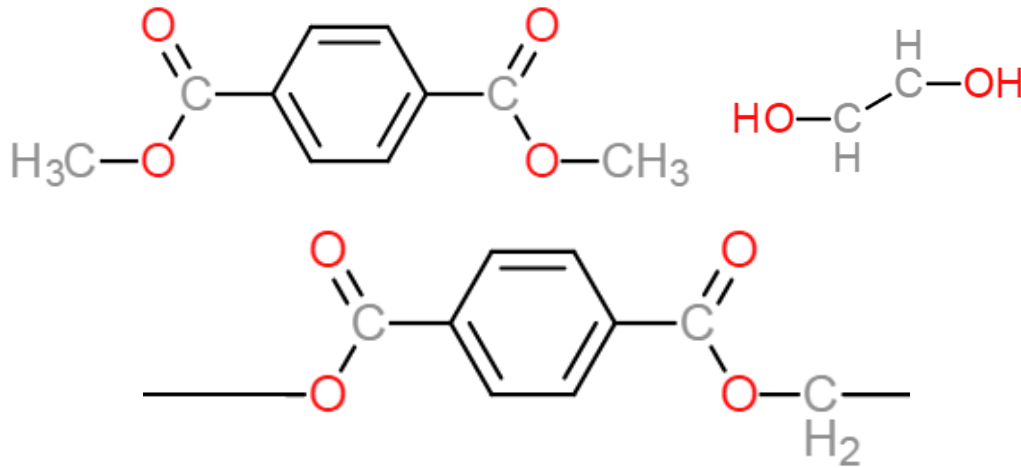


Figure 11: PET monomers and repeat structure

Polyethylene Terephthalate is the commonly recognized polymer used in plastic drink bottles and in polyester fabric. Thanks to its common use, it can be manufactured in many forms and easily recycled. PET can form a highly crystallized structure, but the crystals grow slowly so when PET is cooled quickly it becomes amorphous and appears transparent. As a result FDM parts are usually fairly clear. Printed PET can be easily smoothed by fumed acetone when done safely. It is weakened by hydrocarbons like gasoline, and dissolved by acetone and chemicals with a benzene ring. PET's very high resistance to moisture absorption makes it easy to store for FDM even under humid conditions, and it can be extruded within the normal range of FDM temperatures around 230 °C.

Nylon

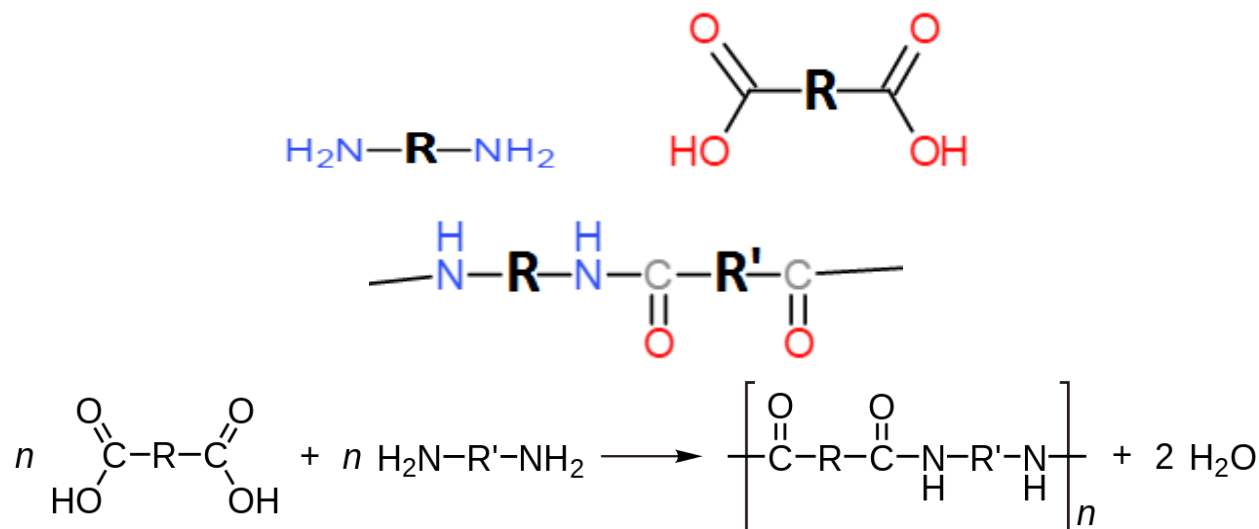


Figure 12: Nylon monomers, repeat structure, and traditionally written polymerization reaction

Nylons are copolymers that start from at least one monomer with carboxylic acid groups at its ends and another with amines at its ends. This means that all nylons have a structure made of whatever was in the middle of the monomer molecules, plus the amide group $-(\text{C}=\text{O})-(\text{NH})-$ in the chain wherever monomers joined. Because whatever is between each set of these bonds is variable, nylon is the name of a family of plastics with widely ranging properties. The properties that make it appealing for 3D printing are its high toughness, flexibility in bending and stiffness in tension, resistance to fatigue, heat and wear resistance, and strong adhesion between Z-layers. However, nylon can warp while printing because of its high coefficient of thermal expansion, it absorbs water from the atmosphere quickly due to the polar amide group, and it tends to be more expensive than other printing materials. For best results Nylons should be desiccated before printing to remove absorbed water. Nylons are generally resistant to solvents like gasoline, acetone, and benzene, but degrade when exposed to acids. Nylon is extruded at high temperatures that may cause damage to some commercial FDM printers, from 240 °C to 270 °C depending on the specific formulation.

Nylon generally has a highly degree of crystallinity due to the aliphatic backbone and polar amide groups. The strength and high processing temperature of Nylon can largely be attributed to the highly crystalline structure. The relatively low T_g indicates that the amorphous regions have good mobility which helps Nylon also exhibit flexibility in addition to its strength from the crystalline regions.

Polycarbonate (PC)

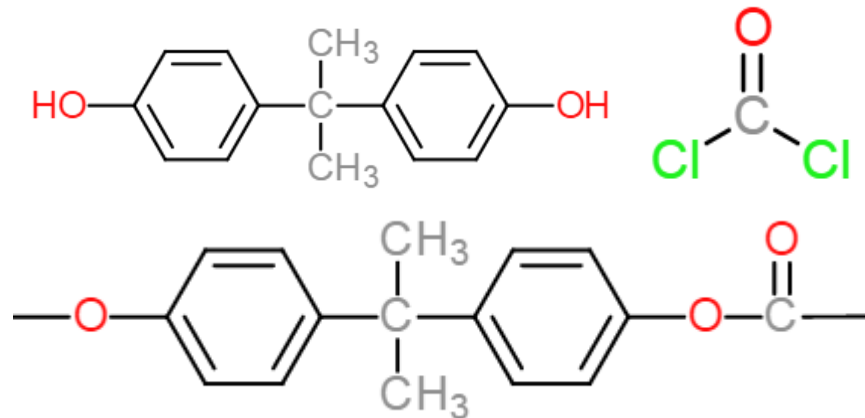


Figure 13: PC monomers and repeat structure

Polycarbonates are technically plastics with the carbonate ester group in the chain, but most polycarbonate plastic is the polycarbonate of bisphenol A. This is the version used in 3D printing and referred to here. Because this is a specific formulation with only one defined repeat unit, polycarbonate (PC) can be expected to vary in properties mostly from the length of the chains synthesized, and not from any of the many permutations that appear when copolymers are involved. PC is used in 3D printing for its high strength and very high Z-layer adhesion, high impact resistance, high toughness, ability to plastically deform greatly before it breaks, high temperature stability, a smooth printed texture, and optical clarity. It doesn't begin to soften until 147 °C, and is extruded at 315 °C, a temperature that many commercial printers cannot reach at all. The drawbacks to printing with PC include the high temperatures required, difficulty adhering it to the build plate, and the fact that it's easily scratched. Acetone embrittles polycarbonate rather than solvating it. Smoothing can be done with MEK solvent, which should be handled extremely carefully. PC is solvated by petroleum chemicals like gasoline and kerosene, and many chemicals with benzene rings and chlorine components, but is resistant to most acids. Polycarbonate can be extruded at temperatures under 300 °C to reduce risk of warping when print bed adhesion is insufficient, but Z-layer adhesion and therefore the strength of the final part will suffer greatly as the bead will not be hot enough to attach to the previous layer well.

Polycarbonate has a highly amorphous microstructure due to the pendant groups and aromatic rings that make the backbone very stiff. These features are also responsible for PC's high strength, optical transparency, and high T_g and processing temperatures. PC will be initially transparent, but will yellow over time from UV radiation that attacks the aromatic rings.

Composite Printing Filament - Plastic Matrix Fills

One way to obtain interesting materials properties in a 3D-printed part is to extrude a composite material. The current most common way to do this with a single print head is to print with PLA filament that contains a certain fraction of fibers or particles which are able to flow with the

melted plastic matrix. Because this introduces another layer of complexity to the possibilities of the material's behavior, care should be taken to follow manufacturer's guidelines and to conduct some research when using these materials. Variations will appear not just in the chain length and composition of the PLA or other matrix used, but also in the chemical composition, shape, size, and amount of the fill material particles. This means that the range of materials behavior is exponentially greater than for simpler combinations. Fill materials are available carrying wood fiber, ceramic particles, brass particles, short carbon fibers, electrically conductive carbon black, and more. In the case of carbon fiber fill, for example, the fibers are hard and abrasive enough that they may erode the inside of an extruder nozzle during printing, slowly increasing the effective nozzle diameter and changing the profile of the extruded layers. Fill materials are generally extruded at the temperature of the matrix component, but the fill material may be affected by the heat as well. In the case of wood fiber fills, extrusion temperature can alter the appearance of the fibers by scorching them, producing shading gradients for aesthetic results. Composite objects should be expected to have stiffness somewhere between that of the matrix and of the fibers or particles, and to change differently during heating. For example, an object made of PLA with brass particles in it will still start to soften around 65 °C, but will require more energy to deform because of the resistance of the brass particles to being pushed through the PLA matrix. A 3D-printed object which is normally vulnerable to abrasion may become resistant after abrasion has exposed tough particles in its surface. Electrical and thermal conductivity, thermal capacity, and resistance to various forms of degradation will also be affected, positively or negatively. It is important to consider all the materials properties that affect the performance of a specific part when printing it with a complex material.

Summary of Properties

Below is a table summarizing key properties of the above material for FDM. As noted above there are many factors that can affect the properties of a polymer so obtaining specifications for materials is usually a good idea if they are available. Optimization of the process parameters for a given material may take some experimentation.

Table 1: Properties of FDM Materials

Property	PLA	ABS	HIPS	TPU	PET	Nylon	PC
Extrude temp. °C	180-220	220-240	220-230	230-260	230-255	235-270	270-315
Bed temp. °C	20-55	80-110	50-60	40-60	55-70	60-80	90-120
CTE (µm/m-°C)	85	68-110	80-90	89-170	60-92	80-95	50-70
T _g (°C)	60-65	105-110	100	-35	70-78	47-60	145-150

Property Definitions

Extrude temp. °C

Nominal recommended temperature of the heater block in the hot-end of the FDM printer.

Bed temp. °C

Nominal recommended temperature of the “build plate” surface on which the FDM object rests. Has a differing effect on the atmospheric temperature depending on how enclosed and insulated the printer is.

CTE ($\mu\text{m}/\text{m}\cdot^\circ\text{C}$)

Coefficient of thermal expansion assumed to be isotropic and measured in units of 10^{-6} distance linear expansion per distance for each degree celsius or kelvin of rising temperature.

T_g (°C)

Glass transition temperature - the temperature or range of temperatures in which a typical sample of the material transitions between a glassy state and a rubbery state. Below this temperature, the material is in a relatively stiff solid state. Above this temperature, the material is in a relatively elastic solid, or supercooled liquid, state. This is a phase transition resulting in a much greater change in the modulus of the material than that caused by normal changes in temperature.

Student Evaluation Questions

1. Why can polymers with the same repeat unit chemistry exhibit a range of strengths and processing temperatures?
2. Discuss how the following characteristics affect properties of a polymer
 - a. Crystallinity
 - b. Amorphous regions
 - c. Polar bonds
 - d. Pendant groups
 - e. Aromatic rings in backbone
3. If a polymer has a significant amount of polar bonds is it more or less likely to absorb water? Why?
4. What properties must a material have in order to be used to make objects in a standard FDM 3D printer? What kind of materials could be used even if the extruder was not heated?
5. What are the advantages of having a heated atmosphere to print in? At what point for a particular material would heating the print bed or printing atmosphere cause a problem?
6. After printing an object from polycarbonate, a user discovers that the extruder jams when attempting to print an object from PLA. What troubleshooting advice would you give them? What materials property are you considering with this advice?
7. If you wished to print an object that could take on new surface textures by having a die pressed on it after being briefly held in boiling water, what FDM materials could you make the object from? Why?
8. While printing ABS and TPU next to each other, you notice that your TPU part sags and fails to support the new layers going on top. After turning the print bed temperature down from your default setting of 90C to 60C, you notice that now your ABS parts fail as one edge curls upwards and sometimes even catches the extruder tip, getting pushed completely out of place. Explain why the ABS part does this.

Instructor evaluation questions:

1. At what grade level was this module used?
2. Was the level and rigor of the module what you expected? If not, how could it be improved?
3. Did the module work as presented? Please note any problems or suggestions.
4. Was the background material on polymer properties sufficient for your background? Sufficient for your discussion with the students? Comments?
5. Did the class generate interest among the students? Explain.
6. Please provide your input on how this module can be improved, including comments or suggestions concerning the approach, focus, and effectiveness of this activity in your context. Send feedback to matedu@edcc.edu.

References

- [1] A. Brent Strong Plastics Materials and Processing 3rd edition, Pearson Publishing, 2005.
- [2] William D. Callister, Jr. and David Rethwisch, Materials Science and Engineering: An Introduction 9th edition, John Wiley and Sons, 2014.
- [3] Lincoln.stl, downloaded from Smithsonian X 3D (<https://3d.si.edu/downloads/27>), educational use, 2017. Original sculptor Clark Mills, 1865.

Bibliography

Plastics, Materials and Processing, by A. Brent Strong. (2005) Pearson Publishing, ISBN 978-0-13114-558-0

Masutani and Kimura 2014, eISBN:978-1-78262-480-6

<http://pubs.rsc.org/en/content/chapterhtml/2014/bk9781849738798-00001?isbn=978-1-84973-879-8#sect466>

Polymer / Solvent interactions taken from:

<http://sevierlab.vet.cornell.edu/resources/Chemical-Resistance-Chart-Detail.pdf>

<http://www.gilsoneng.com/reference/ChemRes.pdf>



This work is part of a larger project funded by the Advanced Technological Education Program of the National Science Foundation, DUE #1501251