MSE – 220

Engineering Materials

Principles of Polymeric Materials

Introduction to Polymeric Materials

Polymeric materials are one of the most important materials for engineering. These materials are used in everything from machine parts to packaging for food. These materials are all of the thousands of polymers and plastics known to the modern world.

Polymeric materials are mostly based from Carbon and Hydrogen atoms with other elements and substances that can be added in. Polymers have been part of nature since the very beginning, animal proteins are polymers along with shellac, rosin, natural rubber and many others. For example, wood is composed of chains of cellulose molecules which are bound together by lignin, which is a natural polymer.

Polymeric materials have only been an important engineering material in the last 75 years. They are a relatively new material for the human race. The first synthetic moldable polymer was cellulose nitrate, or celluloid. This polymer was not very used in the engineering industry. The next generation of polymer were the Phenolic polymers. Phenolic polymers were widely used and started the plastic industry. These polymers were used structurally as well as for to insulate electronic devices. Today light switches are still normally constructed using phenolic polymers.

During World War II, polymeric materials really began to advance at a very rapid pace because of the lack of other materials and the high demand. Nylon was being used instead of silk and vinyl was being used in the place of leather. As of 1979, the tons of plastics being produced exceed the tons of steel being produced.

In this field the term polymer can be used interchangeably with the term plastic, although neither term is technically correct. This is because plastic means pliable, and the majority of polymers are not pliable at room temperature. Polymer is not correct either because its definition is any material made from repeating molecules. For this report as well as in the text book, the term polymer will be used for the chemical formation of the polymer and the term plastic is used for the finished form of these polymers.

Polymerization Reactions

Most polymers are created by long chains of repeating molecules that are linked together via three different reaction types. For these reactions to take place there must a catalyst involved, an increase in temperature or increase in pressure.

Addition Polymerization

In addition polymerization the molecules can be physically linked together link beads on a string. During this reaction the starting material is called a monomer and is in a solution, emulsion, vapor or in bulk. The resulting polymer from the reaction contains chains of the same molecule as the starting monomer. For example, if the monomer was “A”, the resulting polymer would have chains of “AAAA”.

Condensation polymerization

During condensation polymerization two different molecules are attached together through a chemical reaction to form a new polymer chain made up of different molecules the starting materials. For example, if monomer "A" and monomer "B" are forming the new polymer, then, the resulting polymer would consist of chains of "CCCC".

Cross-linking

Cross-linking is not a main type of polymerization but is used by most epoxies to create strong primary bonds. This is where a prepolymer is mixed with a catalyst to form a single macromolecule. For example, catalyst "A" plus prepolymer "B" will result in a macromolecule of "BBB-A-BB-A" and so on.

Polymer Molecules

Polymer molecules consist of Carbon atoms and Hydrogen atoms as a base. The bonds on the Carbon atoms are unsaturated, meaning the molecules are able to bond to other similar molecules to form a polymer chain. To create new polymers, the Hydrogen atoms can be substituted with other elements atom or more complex substance (a substituent or functional group). For example, Polyvinyl Chloride is $CH_2 == HCOH$, one of the H atoms has been replaced by a hydroxyl substituent. If the substituents are very complex, they are replaced by R. The majority of new polymers are made by modifying existing polymers.

Molecular Weight

The weight of a molecule is defined by the length of the polymer chains. The length of these chains can be controlled by processing parameters or by the type of catalyst used. The molecular weight plays an important role in how easily the polymer molds and in the determination of the properties of that polymer. A good technique for measuring the molecular weight of a polymer is to measure the amount of volume of molten polymer that passes through an orifice of given size at a specific temperature in a given amount of time. The volume that can pass through depends on the viscosity of the molten polymer. Because of this we can say that the molecular weight is proportional to the viscosity at a set temperature. The result of this test is known as the melt flow rate. So, the lower the melt flow rate, the higher the molecular weight and the higher the melt flow rate, the lower the molecular weight. This property is known as the melt flow index which is an important property when considering polymer strength. The higher the molecular weight, the stronger the mechanical properties are. Although as molecular weight increases, the processibility decreases.

Chemical Structure

Polymer structures are complex three-dimensional substances. To find out the chemical structure of a polymer, we must first determine the functional groups that make up the polymer. Most analytic laboratories use infrared spectroscopy. In this method the polymer is converted into a film or dissolved into a suitable solution. Then the transmitted infrared energy is measured and recorded. The modern version of this process is, Fourier transform infrared spectroscopy (FTIRS). This new version used a thin film and projects a IR beam and generates a curve from the changes in the reflected beam. On these graphs each functional group is represented by a peak. These peaks are compared to know substances to determine which substances are located in the polymer.

Copolymerization and terpolymers

Copolymerization is the production of a polymer that contains two different monomers. Each monomer can form a polymer but are linking together to form a new polymer that consists of chains of both monomers. The spacing and increments between A and B do not have to be the same. Copolymerization allows for infinite types of plastics with all different properties. Also, most older polymers have been improved using this method. Terpolymers are polymers with three different monomers in its chain.

Alloying and Blending

To create a polymer blend or alloy, at least two different polymers are physically mixed together. At least 5% of another polymer must be mixed to create a blend or alloy. Each polymer added is called a homopolymer, and if the homopolymers are miscible then a single-phase alloy or blend will be created. If they are immiscible then a multi-phase alloy or blend will be created. There are three structures that can be formed. The three are when the additive polymer is mixed with the host polymer, the additive creates spheres in the host matrix, cylinders in the direction of the flow, or lamella (alternating layers). The resultant polymer is an alloy if it behaves as a single polymer, and a blend if it retains some characteristics from its original polymer.

Basic Types of Polymers

Plastics can be divided into two groups

1. Thermoplastic
2. Thermosetting

Thermoplastic

Thermoplastic begins to flow at a high enough temperature and once the polymer is solidified you can reheat and remold the polymer as many times as you want. Thermoplastic polymers usually consist of long polymer chains that is basically a two-dimensional structure. Another name for this type of structure is called linear polymers.

Thermosetting

Thermosetting polymers, once their shape has been solidified, will not be able to melt or flow upon reheating. If you do try to re-melt the material it will either, char, burn or it might even sublime (turn into vapor). The reason it doesn’t re-melt is because when heat and pressure is applied to the material thus causing strong network bonding (polymerization). Thermosetting polymers structure are characterized as a three-dimensional network of molecules.

Classifying Polymers

The 19 most important polymers we need to know is Polyethylene, Polypropylene, Polystyrene, Polyvinyl chloride, Ethenic, Polyamides, Cellulosics, Acetals, Polycarbonate, Polyimides, Polyethers, Phenolics, Unsaturated polyesters, Silicones, Polyimides, Urethanes, Melamines, and Epoxides. There is a very large amount of commercially available plastics that these families provide. To understand each of the plastics you need to first understand the properties of the plastic polymers, and when you understand the properties you will be able to make educated decisions on what type of plastic you should use for your material. In the plastic industry, the industries are very reluctant to give out information on their plastics polymers. They won't even disclose basic polymer system that they used in their grades. There is a specification system has been developed to help identify the types of plastics industries are using. The specification system is called the ASTM D 4000. This shows how a person can employ an alphanumeric identifier for a specific type of plastic. Unfortunately, the system is not widely adopted and will not likely be adopted in the near future. You will need to use generic specifications when necessary if you want to know the types of polymers. If trade names need to be used, you must understand the basic polymers and what fillers and additives it contains.

Linear Polymers

Linear polymers are created by things such as, van der Waals forces, (total intermolecular force) hydrogen bonding, or interaction of polar groups. The polymer chains are usually so flexible they begin to intertwine and lie in a single plane in space. Linear polymers can be amorphous or crystalline depending on their, chain branching, pendent groups or other factors.

Branched Polymers

During polymerization if the chain begins to grow as two chains it becomes a branched structure. Branching causes strengthening and stiffening since the deformation of the polymer needs the chains to be more entwined than the linear polymers. You can control the branches by adding special catalysts and processing techniques, which causes the polymers to have more resilience and can withstand significant stretch without breaking apart.

Cross Linking

Cross linking occurs when during the polymerization reaction the polymers form chemical bonds, and as a result that would make the structure very strong and rigid. This is what happens to most thermosetting polymers. Cross-linking involves primary bonds between the chains. Once the polymer is formed it usually cannot be re-melted because the bonds from the chains are too strong.

Chain Stiffening

Chain stiffening is caused by large substituent groups on the monomers making up a polymer chain. Large substituent groups, like benzene in polystyrene, are referred to as pendant groups. The pendant group size can affect the properties of the thermoplastic. The larger the pendant group means the strength and stiffness would increase. Pendant groups size is also referred to as steric hinderance. Strength and stiffness can also be altered by location. In linear polymers, certain pendent groups along the main chain in a couple different ways. Groups that are placed on one side on the main chain is isotactic. Groups placed on both ends of the chain are syndiotactic. Groups placed randomly anywhere on the chain are atactic. The relative location of the pendent groups is called stereoregularity, stereospecificity, or tacticity. Stereoregularity of the pendent groups can affect the mechanical properties of the polymer. Polymers with greater degrees of stereoregularity, will tend to be crystalline.

Structural and Melting characteristics of Crystalline and Amorphous Thermoplastic

Polymers in the solid state have either an amorphous structure or a crystalline structure. A few factors that influence that affect the structure of a polymer are chain branching, stereoregularity, polarity, degree of cross linking, and steric hindrance. You can characterize the behavior of a polymer by measuring the specific volume in cm^3/g as a function of temperature. An instrument like a dilatometer is used to take the measurements.

- Amorphous Polymers
  - Amorphous materials do not have regular, repeating three-dimensional arrays of atoms.
  - Thermoplastics will favor the amorphous structure if they have large pendant groups, low stereoregularity and extensive chain branching.
  - Thermosetting polymers are amorphous because the cross-linking prevents crystallization.
  - Amorphous thermoplastics melt or liquify over a large temperature range
  - Thermosetting polymers do not melt, but will degrade about a certain temperature transition
  - More dimensionally stable
- Semicrystalline Polymers
  - Polymers that have long, thin aliphatic chains and low levels of chain branching will be more likely to crystalize
  - Most crystalline polymers contain some degree of amorphous polymer
  - Semicrystalline polymers have a defined melting point which is T_m
  - The amorphous phase in a crystalline polymer can have significant effects on the polymers mechanical properties
  - Thermoplastics usually will shrink more than amorphous thermoplastics when cooled from the injection molding temperature.

Additives

Additives improve mechanical properties, thermal processing, surface characteristics, and chemical properties. Additives can be added to polymers in many was like in thermosetting polymers additives are added to the resin through special mixing and dispersion processes. Additives can also be added to a plastic by dispersing polymer pellets or beads that contain concentrated additives into a base resin before they're molded. Polymer pellets with concentrated additives are called masterbatch resins. To improve strength of a polymeric material you can use fillers such as glass, carbon, or aramid fibers. The toughness of a polymer can be improved by incorporating impact modifiers. Lubricant modifiers can cause the polymer to be self-lubricating for wear application, and stop the polymer from sticking to processing equipment or itself when being processed. Plasticizers are added to thermoplastics to improve flexibility and toughness. The most important additives are stabilizers and antioxidants. Stabilizers and antioxidants stops polymers from degrading over time or when they're in use. Additives can also impair some properties while improving another.

Blending and Alloying

Alloying and blending are techniques used to strengthen or later properties. Blending and alloying are cheaper than developing new plastics. If two or more plastics that are going to be blended and they're miscible, (forming a homogeneous mixture) they can form a single-phase material, which is called an alloy. Polymers that are mixed together and are also immiscible will form a two-phase material. The components with the lower concentration will be a separate phase in the other material. The issue with immiscible blends is that the separate phases will most likely have different glass transition temperatures. Another possibility that occurs in blends is that the polymers making up the blend have partial miscibility, which means the types of blends will have more than one phase. To reach the desired blend of polymers there must be a lot of researching and development. Alloying to modify polymers is easier and more cost effective than development for a new plastic. Most blends and alloys are proprietary to specific polymer suppliers, so to gather information of a polymer you would need to conduct a standard test procedure.

Some questions and answers from Ch 9(Polymer Materials)

1. What are the two categories that plastics are divided into?
   Answer: Thermosetting and Thermoplastic

2. Name 4 additives/fillers used in polymers
   Answers: Lubricants, plasticizers, stabilizers, antioxidants, glass, carbon, aramid

3. What are the 4 basic types of polymer chain structures
   Answers: Linear polymer, Branched polymers, Cross-linking polymer, Chain Stiffening polymer

4. What are the 2 main types of polymerization reactions?
   Answers: Addition polymerization and Condensation polymerization.

5. What is the melt flow index?
   Answers: The melt flow index is the property of melt flow rate, which is related to viscosity and molecular weight.

6. What is the purpose of Copolymerization?
   Answers: The purpose is to improve the properties of a polymer by forming a polymer chain from 2 different monomer which are also polymer chains.

7. What are the benefits of Alloying and Blending?
   Answers: They are relatively cheap to develop and take a fraction of the time.

8. For an addition or condensation reaction to take place, certain conditions are needed. What are those conditions?
   Answers: A catalyst, increase in temperature, or increase in pressure.