Plastics Topics – Thermoplastics families

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1. Introduction

There is a bewildering array of plastics materials available in the market today and it is easy to get confused with the number of choices available. IDES (www.ides.com), which provides a search engine and information resources for plastic materials, has more than 85,000 technical datasheets from over 770 separate manufacturers on their database. This is more than enough to allow even seasoned professionals to get lost and confused!

Despite this, there is an underlying order to the apparent chaos and this Plastics Topic attempts to reveal this underlying order, to provide a framework for thinking about the choices and to show that some simple concepts can make things a lot easier.

2. Naming plastics – getting the order right

One of the biggest problems for the industry is the 'alphabet soup' of plastics names and it is easy to get confused when people are talking about PTFE, PMMA, PVC-U and all of the other various types pf plastics. The order in this apparent chaos is cunningly confused by the terminology the industry has traditionally used.

For example, consider High Density Polyethylene (HDPE), Low Density Polyethylene (LDPE), Linear Low Density Polyethylene (LLDPE) and Ultra-high Molecular Weight Polyethylene (UHMWPE). It is not immediately obvious that are all part of the same family (PE). In fact, just reading that sentence probably had most of the readers tongues twisted!

This 'old' naming system grew up with the industry and most of the names grew up in a haphazard manner. This is now changing as chemists and others try to put the most common materials into databases that need to be searched. Under the old naming system, the 'base' polymer name was most often at the end of the name and of the abbreviation, i.e., all of the plastics above are various types of 'polyethylene' or PE. If these were in alphabetical order, they would not be near one another in a database and it would be hard to see the relationship between the materials.

The 'new' naming convention (ISO 1043) is actually quite old but the theory is simple: the base polymer name (or family name) is given first with any modifiers to the polymer after a hyphen. For instance, the examples given above are now:

- PE-HD: Polyethylene - High Density.
- PE-LD: Polyethylene – Low Density.
- PE-LLD: Polyethylene – Linear Low Density.
- PE-UHMW: Polyethylene – Ultra-high Molecular Weight.

This makes the polymers easy to find in any list and categorize into families. The standard international name of any plastic is now in two parts: the basic material or family name is given first and any special properties are given after a hyphen, ALL THE LETTERS ARE IN CAPITALS!

3. Trade names and real names

Another difficulty is that the industry consistently refers to trade names instead of materials types. Nylon is commonly used as the name for materials in the Polyamide family (PA) when the word began life as a trade name for the original manufacturer (DuPont). Equally, Perspex®, Lucite® and Oroglas® are all PMMA by another name and Teflon® is actually a trademark for a specific type of PTFE.

This shorthand is may be convenient for 'those in the know' but it successfully conceals vital information about the plastics and its properties.

4. Family connections

Plastics can be divided up into 'families' on the basis of their chemical structure. A common theme for many Plastics Topics has been how the chemical structure of a plastic determines a wide range of physical, mechanical and other properties. It will come as no surprise that the properties of the members of the major plastics families are therefore all broadly similar. Just as human families share common characteristics, short or tall, thin or fat, light or dark, so the various families of plastics materials share common characteristics. The variations inside a single human family may be very significant but there are still family traits that are shared by most members of the family. Similarly, the variations of any given property within a plastics family may be significant but the broad magnitude of the properties will be distinctive for a given family.

5. Crystallinity – the great divide

Crystallinity is the 'great dividing line between plastics materials and a previous Zeus Technical Whitepaper on "Crystallinity and plastics" discussed the effects of crystallinity. Amorphous polymers (those with no significant degree of crystallization) behave very different to crystalline polymers (those with a significant degree of crystallization). Understanding crystallization and the effect it has on the properties of polymers can make understanding the behaviour of polymer families much easier.

The general properties of amorphous and crystalline polymers are shown in Figure 1:

GENERAL PROPERTIES	
AMORPHOUS PLASTICS	**SEMI-CRYSTALLINE PLASTICS**
• Soften over a wide range of temperatures. • Lower specific gravity. • Lower tensile strength and tensile modulus. • Higher ductility and impact strength. • Lower creep resistance. • Tend to be transparent. • Higher dimensional stability. • Lower fatigue resistance. • Bond well using adhesives and solvents. • Lower chemical resistance and resistance to stress cracking. • Structural applications only (not for bearing and wear).	• Distinct and sharp melting point. • Higher specific gravity due to better packing. • Higher tensile strength and tensile modulus • Lower ductility and impact strength. • Higher creep resistance. • Tend to be translucent or opaque. • Lower dimensional stability. • Higher fatigue resistance. • Difficult to bond using adhesives and solvents • Higher chemical resistance and resistance to stress cracking. • Good for bearing and wear, as well as for structural applications.

Figure 1: The general properties of amorphous and crystalline polymers

Simply knowing if a polymer is amorphous or crystalline will help to define many of the properties and behaviour of the polymer. Understanding crystallinity is truly vital to understanding the behaviour of polymers.

6. Commodity, engineering or performance?

It is also possible to divide plastics families into the relatively arbitrary groupings of commodity, engineering or performance. This gives a broad view of the scale of the mechanical and thermal properties.

'Commodity' plastics have the lowest performance but that doesn't mean that they are weak. Simply that they are cheaper (or more cost-effective as we would prefer to say in the plastics world). These are the bulk polymers that make up over 70% of the production volume of plastics in the world.

'Engineering' plastics have enhanced properties and are used for applications where mechanical or thermal properties are more important. Whilst more expensive, engineering plastics deliver higher performance but represent only about 23% of the production volume of plastics in the world.

'Performance' plastics have the highest mechanical and physical properties of any of the plastics and are used in the most demanding applications. Performance plastics are very expensive and represent about 7% of the production volume of plastics in the world.

These two simple divisions (crystallinity and performance) allow us to classify plastics into one of 6 groups and these are shown in Figure 2. Most plastics families can be located within this broad classification to give a good guide to performance. However, it is important to realize that there will always be variations within a family that 'drift' over into another area, e.g., PE-UHMW and PB (Polybutylene) are both clearly polyolefins but have properties that make them 'engineering' plastics rather than 'commodity plastics.

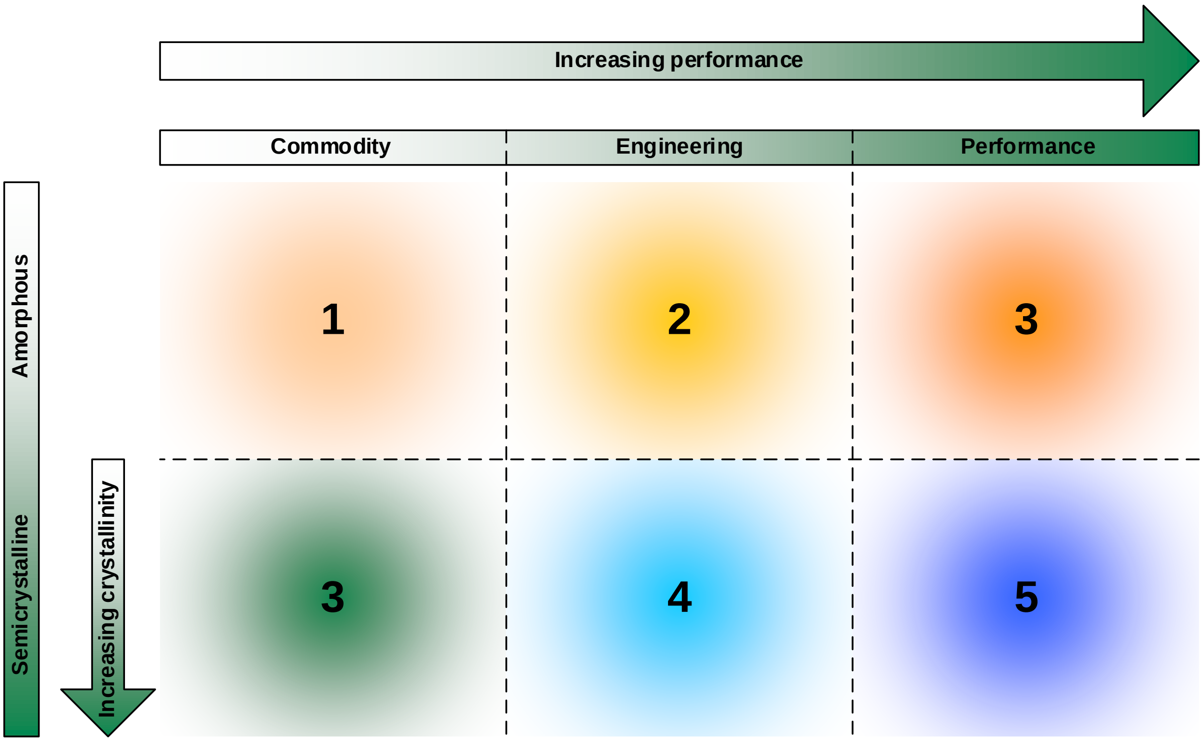

Figure 2: The broad divisions of plastics

7. The Periodic Table of Thermoplastics – a snapshot of polymer families

Locating the various polymer families inside this framework is now relatively easy. This has been done in the "Periodic Table of Thermoplastics" produced by Tangram Technology as a first attempt to provide a simple codification of the basic plastics types and structures to allow the relationship between structure and properties to be seen.

This is called a "Periodic Table" in a nod of acknowledgement to Dmitri Ivanovich Mendeleev who created the "Periodic Table of the Elements", an historic achievement in chemistry that enabled chemists to see the relationship between structure and properties of the basic elements. The 'Periodic Table' concept has now even extended to other areas and it is possible to get a "Periodic Table of Wine", a "Periodic Table of Beer" and even a "Periodic Table of Cheese"!

A reduced version of the 'Periodic Table of Thermoplastics' showing the main plastics families color-coded for easy recognition is shown overleaf and can be downloaded from the Tangram website.

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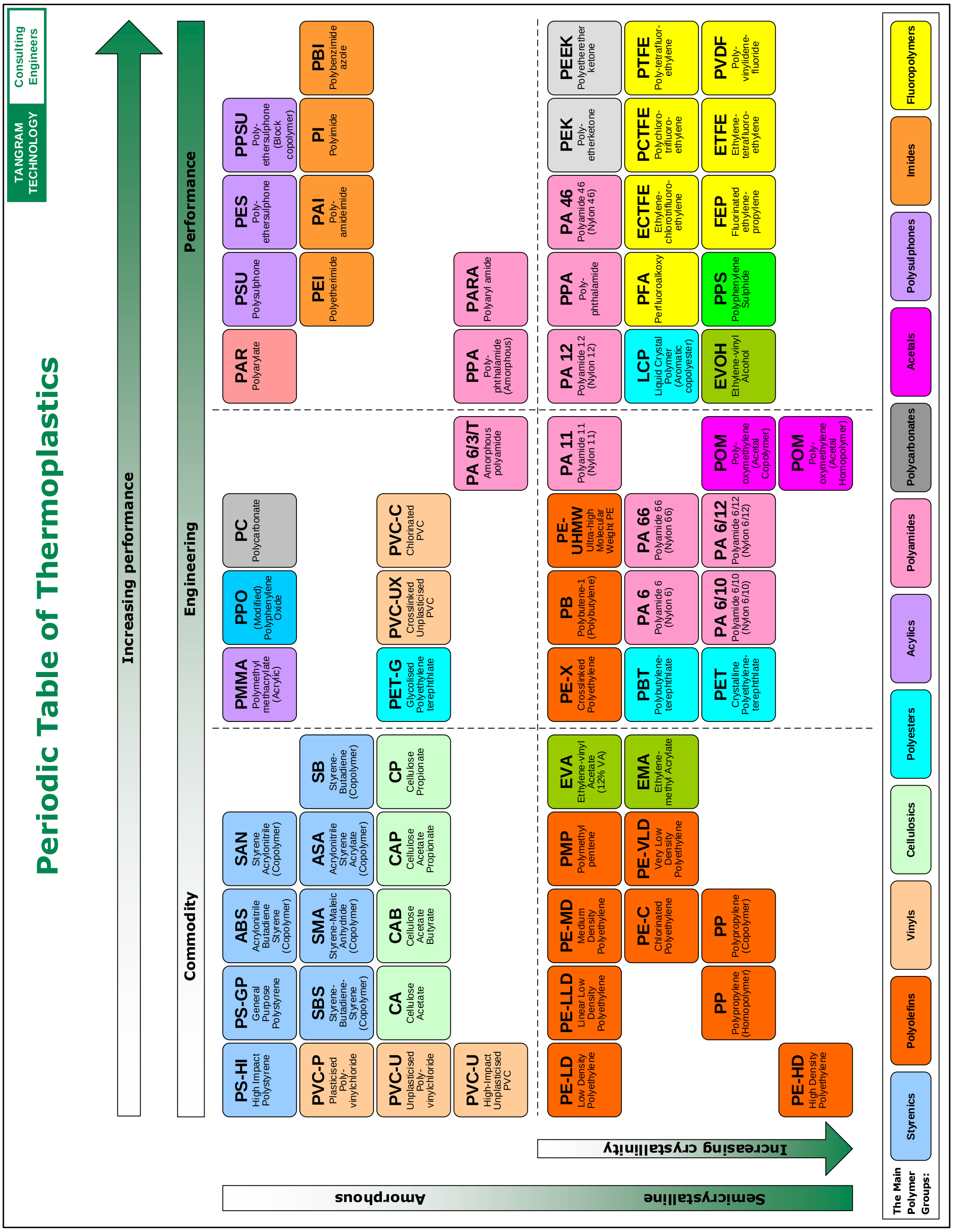

Figure 3: The reduced 'Periodic Table of Thermoplastics'

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The full version of the “Periodic Table of Thermoplastics contains not only the main plastics families but also typical mechanical and thermal data for each plastic. This can also be downloaded from the Tangram website and is shown in Figure 4:

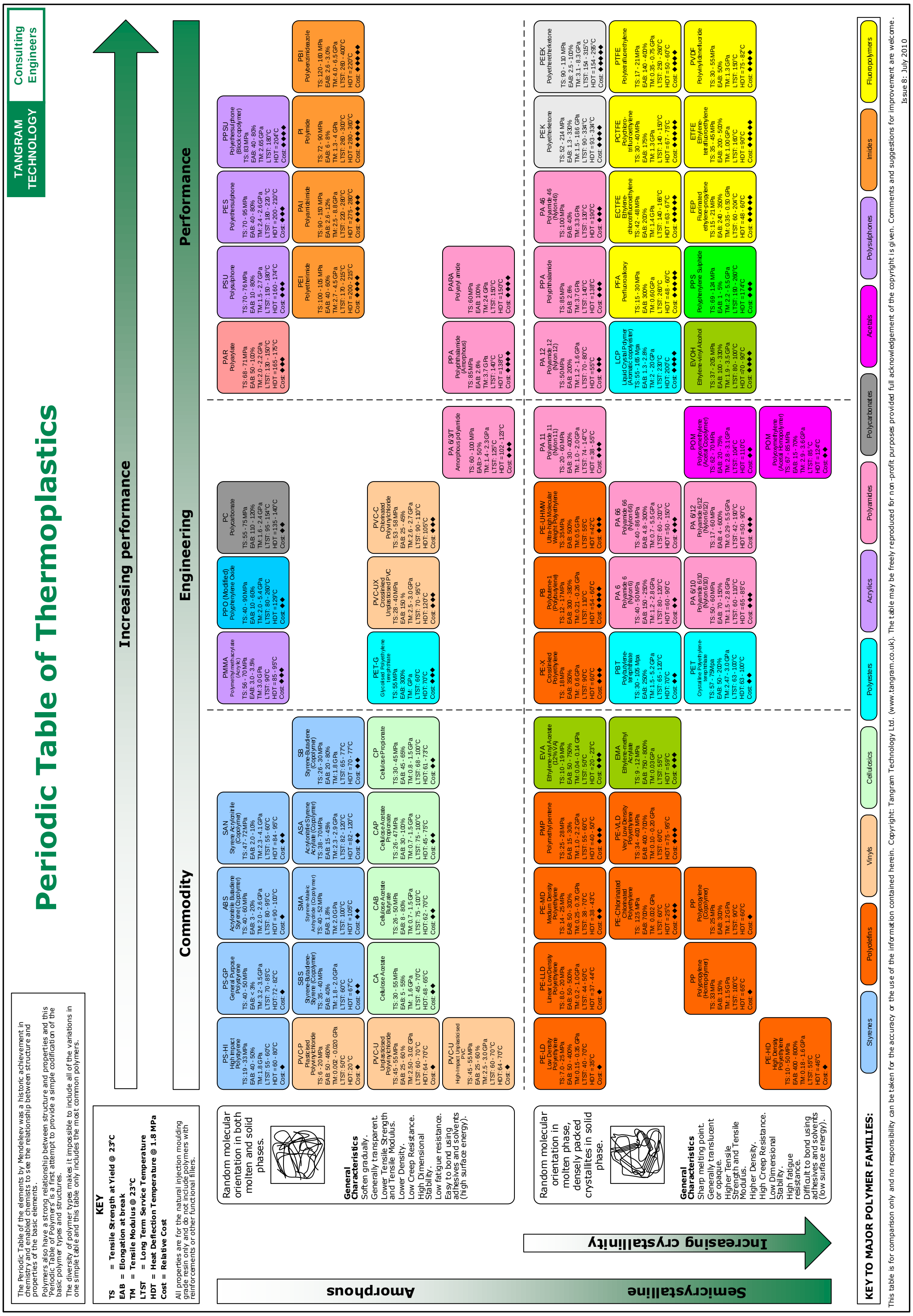

Figure 4: The full ‘Periodic Table of Thermoplastics’

8. The big plastics families

Group 1: Amorphous polymers – commodity plastics

Vinyls

The vinyl chloride plastics are one of the largest families in terms of production volume and are the mainstay of modern life. PVC is one of the most versatile of all plastics because it can be compounded or modified into a wide variety of different states: rigid (unplasticized), soft (plasticized) or pastes. The basic plastic can also be cross-linked or chlorinated to create an engineering plastic with enhanced properties.

PVC – Polyvinyl chloride	
Properties	**Applications**
PVC is one of the most versatile of all polymers. The polymer cannot be used in the natural state but compounding can create an enormous range of properties from rigid products (window frames) through to flexible sheets and hoses. Flexible grades are easy to process. Rigid grades have a high dielectric strength, outdoor stability, chemical resistance, good moisture stability, and low cost. Material has low heat resistance.	Pipes and fittings, wire and cable insulation, window profiles, extruded film and sheet, and medical applications.

Styrenes

The main member of the styrene family is PS (Polystyrene) but the base PS plastic is very brittle and is often modified to a high-impact grade (PS-HI). The styrene family also includes a variety of co-polymers, e.g., ABS and SAN which use co-polymerization to improve the basic PS properties.

PS – Polystyrene	
Properties	**Applications**
Brittle (except in high impact grades: PS-HI), easy to mould, inexpensive, machines well, and possesses excellent transparency. Low mechanical strength.	Inexpensive packaging materials, pens, safety razors, flatware, and CD jewel boxes. In foam format, PS is used to make high-throughput, thin-walled, easy-to-mould parts such as disposable coffee cups.

Cellulosics

The cellulosics are one of the first plastics families and were probably the most important plastics until the 1950s when new plastics were developed. The most commonly known is cellulose nitrate (most famously known as celluloid) but other family members are Cellulose Acetate (CA), Cellulose Acetate Butyrate (CAB) and Cellulose Acetate Propionate (CAP).

The cellulosics have decreased considerably in importance but biodegradability issues are leading to renewed interest in the family.

Group 2: Amorphous polymers – engineering plastics

Acrylics

The acrylics are one of the few clear glass-like plastics and the most common type (PMMA) is known by a variety of trade names for the sheet material. Other plastics members of the family are used for applications such as 'hydrophilic' or soft contact lens. The acrylic materials are not only used for plastics but also for paints, fibres and almost more famously for the production of 'super-glue' or 'cyanoacrylate'.

PMMA – Poly(methyl methacrylate)	
Properties	**Applications**
Hard, rigid, glass clear with good weather resistance and can be used in casting, thermoforming and fabricating.	Signs and leaflet dispensers, automotive lens clusters, lighting diffusers.

Polycarbonates

Polycarbonates are another clear glass-like plastic but have excellent impact strength and are widely used for high-strength glazing.

PC – Polycarbonate	
Properties	**Applications**
Excellent strength and toughness with good dimensional stability, dielectric strength, flame retardancy, and impact resistance (highest among transparent rigid materials). It is susceptible to stress cracking with aromatic solvents, and is difficult to machine.	Riot shields, optical lenses and headlamp sets, vandal proof glazing, medical items, safety helmets, CD's, and power tool housings.

Group 3: Amorphous polymers – performance plastics

Polysulphones/polysulphides

The polysulphones and polysulphides both have a p-phenylene group in the main polymer chain. This stiffens the polymer chain and gives excellent mechanical and thermal performance.

PES – Polyethersulphone	
Properties	**Applications**
This expensive material is electroplatable, has high strength, good toughness, good dielectric strength, and dimensional stability.	Electric connectors.
PPS – Polyphenylenesulphide	
Properties	**Applications**
High temperature resistance (with non-burning continuous use at 240ºC), low temperature endurance, good chemical resistance, and flame retardance.	Chemical pumps, high performance electrical connectors, medical equipment, TV and automotive components and other high stress parts.

Imides

The polyimides are closely related to the polyamides but are amorphous and generally have slightly better properties. In many cases polyimides are modified with ester or amide groups to allow better processing.

PI – Polyimide	
Properties	**Applications**
Rigid, opaque with high impact and dielectric strength, high heat resistance (260ºC continuous, up to 480ºC intermittent), and a low coefficient of thermal expansion.	Bearing materials, thrust washers, and semiconductor wafer clamps.

Group 4: Semi-Crystalline polymers – commodity plastics

Polyolefins

The polyolefins are one of the largest plastics groups in terms not only of the numbers of members but also in terms of production volume where the commodity types alone represent more than 46% of the plastics production. The majority of the family are commodity plastics but some, e.g., Polybutylene (PB) are engineering plastics.

PE – Polyethylene	
Properties	**Properties**
PE-LD/PE-LLD: Flexible, translucent with a waxy feel and has good toughness at low temperatures and low cost. PE-HD: Semi-rigid, translucent and very tough, good chemical resistance with low water absorption and low cost.	PE-LD/PE-LLD: Squeeze bottles, toys, carrier bags sacks and other packaging. Gas and water pipes. PE-HD: Kitchen ware, chemical drums, carrier bags, food wrapping materials. Car petrol tanks.
PP – Polypropylene: the new mild steel	
Properties	**Properties**
High lubricity and high resistance to flexing (living hinges), excellent chemical resistance, good impact strength, and high solvent resistance. Can be sterilized by steam and has good heat resistance. Inexpensive and electroplatable but difficult to paint, glue or print.	Sterilizable hospital ware, medical syringes, beakers, and parts for auto interiors, vacuum flasks.

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Group 5: Semi-Crystalline polymers – engineering plastics

Polyesters

The polyesters are a very large family but most of the production volume is related to PET, the plastic used for the ubiquitous soda bottle and a great deal of rigid food packaging. Polyesters

PET – Poly(ethylene terephthalate)	
Properties	**Applications**
Rigid, clear and extremely tough with excellent dimensional stability and high dielectric strength. Moderate chemical resistance, low resistance to strong acids and bases. Not recommended for outdoor use or in hot water.	Carbonated drink bottles, video and audio tapes, clothing and handles.

Polyamides

The polyamides are also known as ‘nylons’ and whilst not large in terms of production volume they are available in a bewildering variety of variations. The nylons, especially when used with glass-fibre reinforcement, are strong and tough and are ideal candidates for many engineering applications.

PA – Polyamide (Nylon)	
Properties	**Applications**
Rigid translucent and tough with moderate strength. Inexpensive but has poor dimensional stability due to water absorption (hygroscopic nature). Available in many different forms and the mechanical properties can be significantly improved by the use of glass fibre reinforcement. Generally resistant to fuels and oils (dependent on type of PA used). Steam sterilizable.	Gear wheels, zips, bearings, pressure tubing, kitchen utensils and blow mouldings, and clothing fabrics.

Group 6: Semi-Crystalline polymers – performance plastics

Fluoropolymers

The fluoropolymers are also a very large family with broadly similar properties. All have excellent mechanical and thermal properties.

PTFE – Polytetrafluorethylene and other fluoroplastics (FEP, PFA, CTFE, ECTFE, ETFE)	
Properties	**Applications**
Semi-rigid, translucent with exceptionally low coefficient of friction and excellent chemical resistance. High temperature stability (to 260ºC) and low temperature toughness (to -160ºC). Good weathering resistance and electrical properties. Low mechanical strength.	Non-stick coatings. gaskets, packings, bearings, high and low temperature electrical and medical products, other applications needing excellent dielectric strength, chemical, and temperature resistance.

9. Close relations and modifications

The big plastics families reviewed above are obviously not the only types of plastics available and there are many smaller families such as the Polyoxymethylenes (POM or Acetals), Polyphenylenes Oxide (PPO) and the Polyether ether ketones (PEEK). In many cases these can be regarded as distant relations of some of the larger families reviewed and share some of the properties because of their close structural relationship.

It is also important to realize that it is possible to significantly modify the properties of almost any plastic by using a wide range of fillers and additives and that the properties listed above refer to the unmodified base plastic.

10. Summary

The sheer variety and number of plastics available today is almost daunting in scope. However, the chemistry of creating a long-chain polymer means that there are a limited number of methods available that will produce a viable plastic. These methods define the structure of the resulting plastic and create a limited number of plastics 'families'.

The close relationship between structure and properties means that knowing the family of a given plastic allows a broad range of properties to be rapidly deduced or predicted.

As a final note, my favourite polymer is PPTKO otherwise known as "Polly Put The Kettle On".