

1

Introduction

High-performance or specialty thermoplastics (STPs), both amorphous and semi-crystalline, are plastics that can withstand high temperatures, usually higher than 150 °C, for long periods of time; they have mainly aromatic rings in the polymeric chains, which enable them to exhibit these characteristics and, therefore, have outstanding mechanical properties, have ether or sulfide groups to make them flexible and processible, and have sulfone, ketone, or imide groups (except for PPS) to promote some special properties. Among commercially available specialty thermoplastics, amorphous polysulfone (PSU) with a glass transition temperature (T_g) of 179 °C is at their lower end and semi-crystalline polyether ketone ketone (PAKK) with a melting point (T_m) of 395 °C is considered at their higher end. Other polyaryl ether sulfones (PAES), polyetherimides (PEI), polyphenylene sulfides (PPS), and polyaryl ether ketones (PAEK), are in between these two ends. Figure 1.1 shows a thermoplastics pyramid including the higher positions of the STPs discussed in this book.

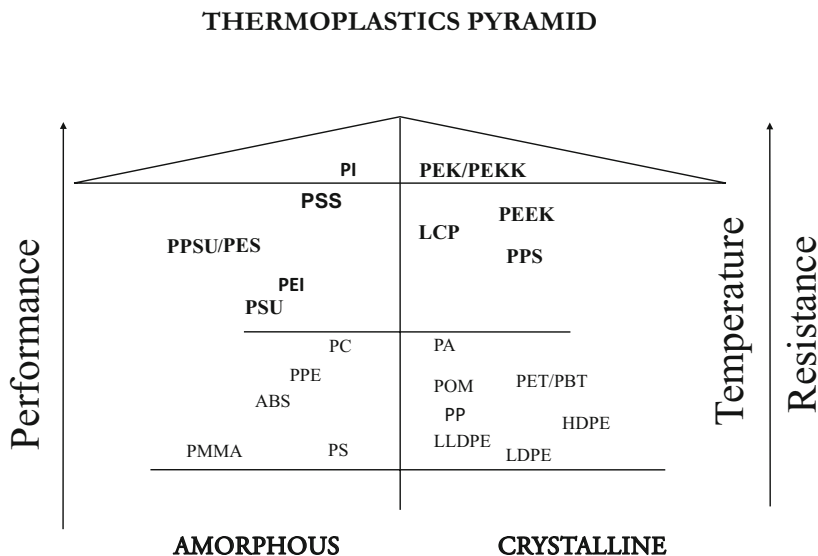


Figure 1.1 STPs positions in plastics pyramid

1.1 Technical Requirements

What are the characteristics of specialty thermoplastics and what are their challenges for commercialization? There are, of course, hundreds of structures of aromatic polymers that may qualify to be called STP based on their T_g (> 150 °C) or T_m (> 250 °C) criteria, but their commercialization poses formidable challenges. These plastics should not only have a high T_g or a high T_m , but also excel in other important properties for making a successful entry into the market space. Chief among these are high-temperature melt stability for processing, high shear resistance without degradation at these processing temperatures, good rheological characteristics, high mechanical properties at elevated temperatures, excellent resistance to chemicals, radiations, and wear and tear, good electrical properties, and, finally, right economics for commercialization.

As can be seen in Table 1.1, the commercially established specialty plastics have high T_g or high T_m .

Table 1.1 Thermal Properties of Specialty Plastics (STP)

STP		T_g , °C	T_m , °C
PSU		179	NA
PES		224	NA
PPSU		222	NA
PEI		217	NA
PPS		85	285
PEEK		145	335
PEK		163	365
PEKEKK		170	381
PEKK, T/I %	60:40	158	305
	70:30	163	335
	80:20	165	370
	100:0	175	395

All these commercially produced and available plastics are readily classified as specialty thermoplastics. Interestingly, some of these may also be available in a variant, where they exhibit higher T_g or T_m with comonomers added or made as thermosets to get cross-linked under high heat exposure. These variants are also briefly covered in this book. However, the scope of this book is restricted to only four main groups of STP, polyaryl ether sulfones (PAES), polyetherimides (PEI), polyphenylene sulfides (PPS), and polyaryl ether ketones (PAEK).

It is easy to note that these four STPs fall into two main groups: While PAES and PEI are amorphous, PPS and PAEK are semi-crystalline. These all are largely linear polymers with no or little branching, except for PPS, which can be branched or linear. Further, they are mostly *para-para* (PAES, PPS, PEEK, PEK, PEKEKK) or *para* and *meta* (PEI, PEKK) covalent bonded polymers. The difference in the size of $-SO_2-$ and $-O-$ groups, with spatial requirements, does not allow close packing of their attached phenyl rings, making PAES amorphous. Similarly, in the case of PEI, its three substitutions on a phenyl ring keep it from being crystalline and hence PEI remains amorphous. On the other hand, the simple mainly *para-para*-linkage of $-S-$ in PPS and the near steric equivalence of $-O-$ and $-CO-$ groups, allow close packing of the phenyl rings of PAEK, make them semi-crystalline structures.

■ 1.2 Production

All specialty plastics are made using nucleophilic substitution or electrophilic addition reactions using a single or two, or even three, mostly aromatic monomers. The linkages joining these aromatic rings are $-O-$, $-S-$, $-CO-$, $-SO_2-$, $-C(Me)_2-$, $-C_6H_4-C_6H_4-$, or $(-CO)_2N-$. Depending on the presence of these linkages, properties of STPs undergo change. The polymerization reactions are carried out usually in an aprotic solvent, at temperatures from somewhat less than ambient temperature of 0 °C to 75 °C for PEKK, to less than 200 °C to 220 °C for PEI and PAES, to near 270 °C for PPS, and to as high as 320 °C for PEEK and PEK. Getting reactive end groups capped and getting rid of by-products, usually metal salts and water as well as, of course, the solvent used itself, is as challenging as controlling the chain structures and molecular weights of these polymers. Importantly, these reactions being step-growth polymerizations (as against chain-growth for vinyl monomers), for attaining high molecular weights, the conversion of monomers needs to be usually higher than about 99.00%, following Carothers' equation $DP = 1/1 - p$, where DP is the degree of polymerization and p is monomer conversion. This forces extremely high purity requirements for monomers, solvent, and any other reactant used in polymerization (PZN).

Historically, the growth of STP was somewhat slow, requiring several years to grow from lab scales to commercial scales. Thus, PES/PSU as well as PPS were first developed in the 1960s but only fully commercialized in the 1970s. Similarly, PEI and PEEK/PEK were developed in laboratories in the 1970s but only were commercialized in the 1980s [1]. PEKK was developed in laboratories in the 1950s but was fully commercialized in the 1990s and later.

Major producers of these four groups of specialty thermoplastics are Solvay, Ticona, Sabic, Arkema, BASF, Evonik, Sumitomo, Victrex, DIC, Kureha, Teijin, SK Chemicals, Toray, UJU, Pengin, and Gharda. They produce STP mainly in the USA, France, Japan, China, South Korea, and India.

Table 1.2 gives these specialty thermoplastics, their manufacturers, locations, and known production capacities.

Table 1.2 Producers of STP and Their Capacities

Producer	STP	Location	Total Capacity,* MTA
SOLVAY	PSU, PESU, PPSU	USA	55,000
	PESU	India	
BASF	PSU, PESU, PPSU	Germany	22,000
	PSU, PESU, PPSU	S. Korea	
SUMITOMO	PESU	Japan	2000
UJO	PSU, PESU, PPSU	China	1000
SABIC	PEI	USA/Spain	25,000
SOLVAY	PPS	USA	12,000
TICONA	PPS	USA	12,000
DIC	PPS	Japan	20,000
KUREHA	PPS	Japan	10,000
TEIJIN	PPS	Japan	5000
TORAY	PPS	S. Korea	8600
INITZ	PPS	S. Korea	6000
VICTREX	PEEK, PEK	UK	7000
SOLVAY	PEEK	India	2000
		USA	
EVONIK	PEEK	China	1000
PENGIN	PEEK	China	1000
SOLVAY/RALLIS	PEKK	India	100
ARKEMA	PEKK	France/USA	1200
POLYMICS	PEKK	China	50
GHARDA	PEK, PEKK	India	200

* As given on company website or as known in market; MTA = metric tons per year.

Thus, these STPs are being produced by only a few companies and only in a few countries of the world.

The major three polysulfones, PSU, PES, and PPSU, are produced by Solvay in the USA, and PES also in India; BASF produces PSU, PESU, and PPSU in Germany and

in South Korea; Sumitomo produces PES in Japan; and UJU produces PES, PSU, and PPSU in China.

Sabic is the sole producer of PEI in the world, with plants in the USA and Spain.

PPS is produced by Ticona and Solvay in the USA; by Teijin, Kureha, and DIC in Japan; and by Toray and SK Chemicals/Teijin (INITZ) in South Korea.

PAEK are, interestingly, produced by a number of manufacturers now. Victrex, the pioneer for PEEK, has a production plant in England. Victrex also manufactures PEK and has recently also started production of PEKEKK in England. Solvay has a PEEK plant in India and has recently started a second plant in the USA. Rallis (now for Cytec/Solvay) and Gharda produce various PEKK grades in India. Gharda also manufactures PEK in India. Evonik manufactures PEEK in China as also Pengin has its PEEK plant in China, whereas Arkema manufactures PEKK in France, with a second plant having been commissioned recently in the USA (Table 1.2).

India takes pride of place among other countries producing PAEK, with Solvay (PEEK, PES, PEKK) and Gharda (PEK, PEKK) having their production plants in the Ankleshwar, Panoli area in Gujarat since the early 2000s.

■ 1.3 Processing of STP

Specialty thermoplastics are generally processed using all common thermoplastics processing techniques, particularly extrusion and injection and compression molding. In some cases, blow molding and roto-molding are also possible. The latest processing technique for STP is additive manufacturing or 3D printing, which is being used for nearly all STPs.

These processes can be used directly for powders or for filled or unfilled granules, for converting STP into a variety of articles.

1.3.1 Powder Processing

The thermoplastic powders can be directly used for coatings, for solution-based sheet or hollow fiber membrane preparation, and for compression molding.

Coatings can be prepared also in solutions by dissolving the powder in a given lower boiling solvent (only amorphous STPs are easy to dissolve) or by preparing a water-based suspension. Direct powder coating can also be used. If STPs are available as melt-based granules directly, like PEI, for example, they may be required to be ground into powder before using them for these processing techniques. After

applying them to a surface, generally, coatings need to be baked or cured at high enough temperatures to melt and give a strong, adhering film on the coated substrate.

Membrane application also preferably needs powdered STP, particularly of PSU or PES, since powders dissolve more quickly than granules in a given solvent. It is then wet spun into water to give hollow fibers or flat membranes.

1.3.1.1 Compression Molding

Compression molding is carried out mainly using powders, as the use of granules generally leaves their border marks on the molded articles.

Compression molding may need a long-time cycle. This requires compacting of STP powder in a mold, heating it slowly to the desired high temperatures, and holding it under pressure for a time to form a homogeneous mass. The powder may be dry blended with heat stabilizer, antioxidant, colorant, powdered glass or carbon fibers, and any other additives, before transferring it to the mold. After the required time under the needed pressure is over, the heat is turned off and the mold is allowed to cool, and the article is removed once the temperature reaches ambient level or at least it is well below the T_g of the molded polymer. In some cases, after the compacting in press, the mold with a locking arrangement is transferred to an oven at a higher temperature and melted. To avoid any void formation or splay marks, it is advisable to open the mold while compacting and heating, in order to get rid of any entrapped air and volatiles.

Even though compression molding is a slow heating and cooling process, generally requiring several hours of operations, the articles so produced further need to be annealed to get built-in stresses removed, which is another operation that lasts a few hours. The annealing time cycles are similar to that for molding, but the temperatures used are slightly lower than T_g for amorphous STPs but higher than T_g and lower than T_m for semi-crystalline STPs.

Compression molding is extensively used when the number of articles to be produced is low. Further machining may be required to get the flash out or make the surface smooth. It is a popular technique for producing seals, valve seats, and other general engineering items.

1.3.1.2 Powder Extrusion for Compounding

Since many specialty plastics, such as PAES, PEI, PPS, and PAEK, are manufactured in solutions, on precipitation in a non-solvent they form powders, while PEI is directly devolatilized in an extruder and the melt is converted into granules. The powdered plastics need to be extruded first into pellets, using a co-rotating twin-screw extruder. They are first usually, though optionally, dry blended at the powder stage with any required additives like lubricant or stabilizer, colors, and/or

other fillers for improving any special properties before extruding. STPs are usually so thermally stable that it may not be necessary to add any heat stabilizers before extruding for granulation. Dry blending usually is carried out in a high-speed mixer for 15–20 minutes with temperature starting at ambient temperature but reaching 50–60 °C due to frictional heat. All required powdered additives are charged along with the polymer powder to the mixer.

Dry blend so prepared is then extruded in a co-rotating twin-screw extruder for further mixing as well as for melting and devolatilizing. The addition of reinforcing fillers like glass fiber (GF) or carbon fiber (CF) is carried out at this stage, after melting the powders. Often, it is carried out using already prepared natural granules instead of a dry blend. Using granules adds to the heat history of the final compounds but has the advantage of a better homogenization when the fiber percentage is high like 30% or even higher. It also gives a higher output than that obtained using powder. A twin-screw extruder typically has seven to ten zones, plus a die zone. The screw and barrel liners are made using hard corrosion-resistant metal to withstand wear at high temperatures due to the high-viscosity melt, frequently with abrasive CF and GF added to it.

Besides a feeder for powdered resin, there can be a second feeder for additives, and a third feeder for stapled CF or GF addition, after the resin has melted. This helps in keeping CF or GF from getting too crushed due to less compressive screws at that juncture. One can also add CF or GF filaments or roving directly, which get broken down to smaller pieces during compounding in the extruder.

The first two zones of the compounding extruder are feeding zones and for deaeration, where air coming in, along with powder, is removed and the powder is compacted.

The next zones are meant for melting of powder. Melting zones also make a homogenized mix of the polymer with the different additives added. After that, GF or CF may be added to the melt in later zones, giving enough torque to mix but not so much as to break the fibers excessively.

The melt, with reinforcing agents, if any, is then passed through zones for devolatilizing it with applied vacuum. Polymer powder may contain 0.2% to 2.0% or more volatiles like moisture, solvent, monomers, low molecular weight oligomers, etc. Often, more than one barrel has these devolatilizing ports. Care needs to be taken that the polymer is completely melted when passed through these barrels, as otherwise polymer powder may also get sucked out due to the high vacuum applied. Some systems, possibly for PEI, are known to have six or seven vacuum degassing ports attached to the extruder to flush 25% or more of solvent remaining in the polymerized reaction mass, in order to take out melted polymer with essentially less than 100 ppm of solvent.

The final zones usually carry the material to pump out the compound so produced into strands through a die, which are then water- or air-cooled and then chopped into granules. The die design is important to give shape to strands, usually round but can also be square, as well as to decide how many strands can come out of a given die. This optimum number of holes and their sizes are important to give a uniform-size output, while too many holes may make outer strands thinner. The final size of strands, and therefore of granules, depends also on the shrinkage or die swell of a given polymer composition as well as on the rollers placed on the granulator pulling these, water- or air-cooled, strands.

The rpm of screws is as high as 250 and the high vacuum applied for degassing may reduce pressure to 700 mmHg inside the extruder. The output, of course, varies from polymeric system to system, with its bulk density, powder flow, and volatiles to be degassed, apart from the dimensions of the extruder itself. It varies, in particular, depending on whether powder or granular STP is compounded. For natural, unfilled STP powder, since more devolatilizing is generally needed, the output is smaller. Granular STP in compounding shows a greater output because of its higher bulk density and lesser need for devolatilizing, allowing faster extrusion. Additionally, fillers further increase the specific gravity, thereby also the output substantially. The output for granular STP with fillers added can be as much as 30–100% higher than that for unfilled STP powder.

The compounded mix is then pushed through a die head with several holes, to be pumped out as strands. The number of holes on a die head can vary from one or two to twenty or more, depending on the machine capability and the polymer melt viscosity. The strands, coming out at temperatures of 350–400 °C need to be cooled, usually in a water bath before sending them to be cut down into granules.

There are several types of cutters or granulators available for this. The simplest and most used are strand cutters, where strands are first cooled in a water trough and then cut into granules using a separate pelletizer. One can also use a water ring pelletizer, where the die head is a circular die with holes and a rotating knife cuts the strands right when they come out, and the granules are immediately plunged into water for cooling. The main difference between the two is that in the first case, cooling takes place before cutting. In the second case, they are nearly simultaneous. Another difference is in the shapes of granules, depending on the shape of die holes. The first one gives cylindrical or cubical granules, while the second one yields spherical granules. The speed of cutters generally decides how big or small these granules are. Additionally, the diameter of the die head holes and any stretching taking place after coming out of the die also affect the granules' size and shape.



Figure 1.2 Shape of PEK granules

A third popular method of granulation is the use of a water-submersed die, or underwater pelletization, where the entire die is inside the cooling water bath, unlike in the water ring pelletizer, where water circulates around the die, without immersing it. This is more commonly used for commodity and engineering plastics, where extrusion temperatures are much lower than in the case of specialty plastics.

The granules so produced are collected, dried further, if needed, and then packed or stored in a silo for further use or packing.

Figure 1.3 shows a schematic design of a twin-screw extruder line from Coperion GmbH.

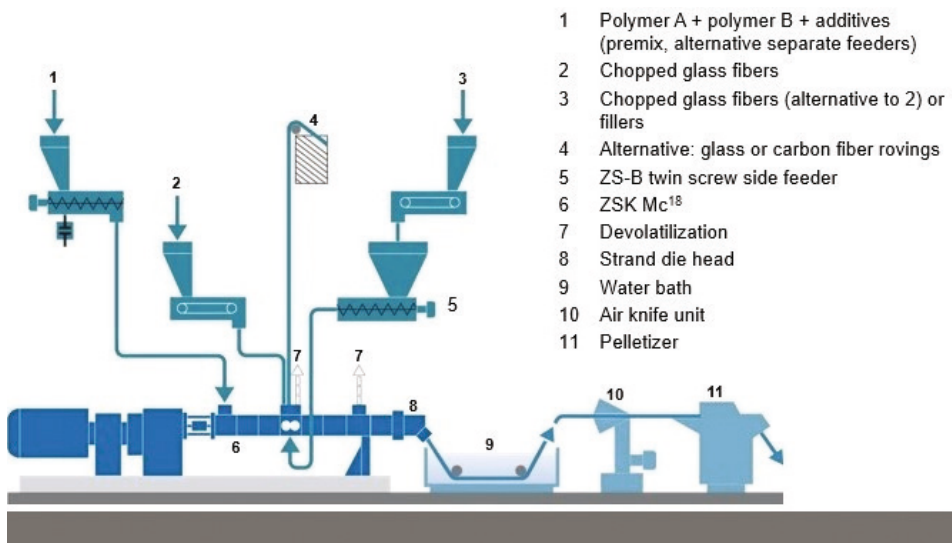


Figure 1.3 Compounding line for STP.
Courtesy of Coperion GmbH, Germany

Figure 1.4 shows a normal twin-screw design for such a compounding extruder. Both the barrel and the screws are segmented, unlike most single-screw extruders, which come in one piece. This allows for barrel segments of different configurations, like having inputs for polymer and fillers, for applying vacuum, etc. The segmented screws come in many shapes and sizes. The shape of the screw elements first allows deaeration as well as compacting powders into melts, then homogenizing with additives, if added separately, then mixing with GF or CF, and, finally, devolatilizing and then pumping out the compound through the die.

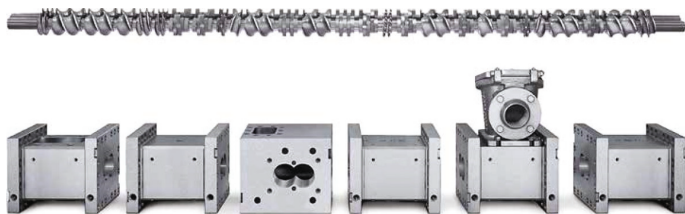


Figure 1.4 Drawing of segmented twin-screws and barrels.
Courtesy of Coperion GmbH, Germany

More details of compounding conditions are given in the respective STP chapters. The major processing techniques for the granules of STPs are extrusion and injection molding. These require a single-screw extruder, with, optionally, a melt pump, and with suitable dies. Other ancillaries used are sizing units and takeoff units with cutting units, for extrusion, and hot-runner system and auto-takeoff units, both optional, for injection molding. More details of these as well as other processing techniques as applicable will be discussed in the individual chapters.

Specialty plastics can be extruded into strands, pipes, rods, plates, profile shapes, and also as films, fibers, and cable insulation.

1.3.2 Processing of STP Granules

STP granules, filled or unfilled, are mainly processed by injection molding or extrusion. Injection molding uses almost 70% to 80% of STP granules for myriad applications. The extruded rods, pipes, and profiles, also termed stock shapes, use up to 30% of STP, particularly of PEEK.

Injection Molding of STP

Typically, amorphous plastics are processed at temperatures higher by 120 °C to 150 °C than their T_g . Thus, PSU, PES, PPSU, and PEI need processing temperatures of 350 °C to 380 °C. On the other hand, for semi-crystalline plastics, the tempera-

tures needed are 20–30 °C higher than their T_m . Details of specific conditions are given in the respective STP chapters. Figure 1.5 shows a typical injection molding machine from Arburg GmbH.



Figure 1.5 Injection molding machine.
Courtesy of Arburg GmbH, Germany

Typical injection molding machines for STPs are smaller, with single- or multi-cavity molds. In general, due to high melt temperatures of 350 °C to 410 °C and the high melt viscosity, particularly of filled grades of STP, both the barrel and the screw should be hardened or nitrated and be abrasion- and corrosion-resistant. Nowadays, electrical heating of these is preferred. Hot runners are usually not used due to the high temperatures involved. Mold temperatures are important to get complete filling, little or no flash, and internal-stress-free articles. The mold temperature also determines the crystallinity of the molded articles for PPS and PAEK. Too low a temperature of mold, below their T_c , would lead to quenching and hence amorphous, transparent to translucent objects, while the temperature being above T_c would allow crystallinity to be built up, giving opaque articles. Mold temperatures above T_g for amorphous STP and above T_c for semi-crystalline STP would lead to insufficiently cooled articles, prone to warping. Robotic handling of molded articles for picking them up from the mold and depositing them on a belt to be carried forward is becoming common.

■ 1.4 Properties of STP

The first test for checking whether a given polymer is an STP or not, whether it is worthy of commercialization or not, is to evaluate its resistance to higher temperatures as required by the processing temperatures in common techniques such as injection molding or extrusion. Prevention of cross-linking is highly important when

processing at such high temperatures. Other degradation mechanisms are also prevalent, like reduction in molecular weights, branch formation, any labile groups on polymeric chains getting flashed off, and the very common discoloration. Some of these may be caused on the polymer chains themselves or can be due to trace impurities contaminating these polymer chains. Hence, besides a robust chain structure, STPs should have the highest purity to remain without any side reactions.

Simple thermogravimetric analysis (TGA), in N_2 or air, can give a good indication of the thermal stability of the polymer chains under static conditions by showing weight remaining constant up to a given high temperature. All the specialty plastics discussed here show virtually no major weight loss up to 400 °C to even 500 °C, and some show no weight loss up to even 550 °C. Figure 1.6 shows TGA curves exhibiting the superior thermal stability of PEK, for example, as compared to an engineering plastic like polycarbonate (PC). PC starts degrading heavily at 460 °C (initial degradation temperature, IDT), while PEK shows an IDT of 564 °C, a clear 100 °C advantage [2].

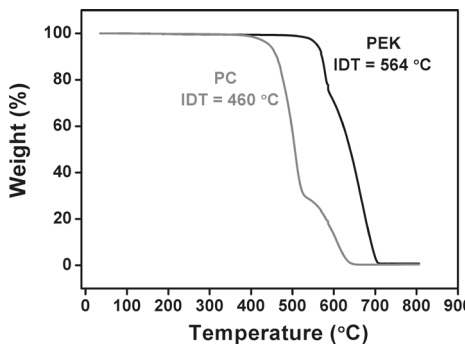


Figure 1.6
Typical TGA curves of PEK and PC [2]

The thermal stability under static conditions as in the TGA measurement is one important part of its evaluation. A more stringent evaluation is to have melt stability under differing shear rates and temperatures. These tests are performed using myriad rheological instruments, starting from the humble melt flow indexer (MFI) or the capillary rheometer (CR) to the more sophisticated parallel-plates rheometer, or even a rheometer simulating actual processing conditions, such as a Haake- or Brabender-type rheometer. Here, one can keep the shear rate and temperature of processing constant or varying as desired, and measure the melt viscosity changes as a function of time. Depending on the polymers and test conditions, it is expected that melt viscosity remains constant or within a 20% variation approximately for 30 to 60 minutes of tests, for STPs. This is an important test to be cleared before launching any specialty polymer into the market. Figure 1.7 shows the melt stability of PEEKs of high and low molecular weights as a function of time, indicating excellent stability at 400 °C in a capillary rheometer at a shear rate of 1000/s [2].

Index

A

ABS 16

E

electrophilic
- technology 22

G

Gharda Chemicals 77

I

imidation 79

N

nucleophilic
- etherification 79
- technology 22
nylon 6 16

P

PAEK 148
- electrophilic polymerization 154
- medical applications 224
- nucleophilic polymerization 153
- PEKEKK production 161
- PEK production 158
- performance 217
- production 156
- Victrex 148
PAES
- 3M 22

- blends and alloys 32
- block copolymer 24
- compounding 37
- CUT 45
- DCDPS 23
- DHDPS 23
- electrical properties 63
- electrophilic polymerization 28
- extrusion 39
- food and medical applications 66
- Gharda Chemicals 22, 24
- injection molding 39
- ITD 44
- manufacture 21, 24
- mechanical properties 47
- membranes 33
- nucleophilic polymerization 25
- optical and chemical properties 41
- performance 65
- powder coating 34
- powder processing 32
- processing 38
- properties 41
- reactive PESU 31
- recycling 63
- rheological properties 61
- Solvay 22
- T_g 44
- TGA 44
- thermal properties 44
- thermomechanical properties 57
PC 16
PEI 77
- additive manufacturing 89
- compounding 87
- crystalline 82

- electrical applications 112
- etherification 79
- Extem 78
- Extem 3D printed 91
- extrusion of stock shape 87
- fiber spinning 92
- filament extrusion 88
- films 93
- GE Plastics 77
- Gimide resins 79
- imidation 81
- injection molding 93
- melt polymerization 83
- performance 106
- polyamic acid 77
- powder processing 86
- preparations 79
- processing 86
- production 84
- properties 94
- rheological properties 104
- Sabic 77
- Siltem 78
- single monomer 83
- Stratasys 89
- thermal properties 101
- thermomechanical properties 102
- Ultem 77
- Ultem 9085 90
- PESU
 - Astrel 22
 - of high T_g 55
 - Radel A 21
- polymerization 3
- PP 16
- PPS 21, 115
 - coating 125
 - compounding 128
 - compression molding 128
 - crystallinity 134
 - curing 122
 - extrusion 133
 - fiber 132
 - injection molding 129
 - mechanical properties 138
 - performance 140
 - powder processing 122

- preparation 116
- processing 121
- production 120
- properties 133
- reaction mechanism 118
- rheological properties 139
- thermal properties 135
- PPSU
 - Radel R 21
- preparations 25
- PSU
 - Udel 21

S

- STP 1, 21
 - advantages 19
 - amorphous 1
 - Arburg GmbH 11
 - Coperion GmbH 9
 - HDT 14
 - IDT 12
 - LOI 15
 - marketing 18
 - PAEK 21
 - PEI 21
 - performance 18
 - PESU 21
 - plastics pyramid 1
 - PPSU 21
 - processing 5
 - producers 4
 - production 3
 - properties 11
 - PSU 21
 - semi-crystalline 1
 - smoke density 15
 - specific flexural modulus 17
 - thermal properties 2

T

- TGA 12

U

- Union Carbide 21