

Prakash D.Trivedi

Specialty Thermoplastics

Preparations, Processing, Properties, Performance



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Dedication

Respectfully and affectionately dedicated to my two gurus:



My mentor, Dr. Keki H. Gharda,
Chairman & Managing Director,
Gharda Chemicals Ltd., Mumbai, India.



My guide, Prof. Dr. Joseph P. Kennedy,
Distinguished Professor of Polymer Chemistry,
Institute of Polymer Science,
The University of Akron, Ohio, USA.

The Author

Prakash Trivedi obtained his master's degree in chemistry from the University Department of Chemical Technology, University of Bombay, India and his Ph.D. from the Department of Polymer Science, University of Akron, Ohio, USA. He has worked with research departments of companies such as Firestone, IPCL, NOCIL, Rishiroop, and Apar Industries. He was Head - SBU Polymers at Gharda Chemicals Ltd. from 1990 until 2006 and from 2011 to date developing mainly specialty plastics. He was managing director of Solvay Specialties in India from 2006 to 2009 and a member of Advanced Technology at Solvay from 2009 to 2011.



Prakash has co-authored the book "PVC Technology" and has published more than 90 papers and presentations in national and international journals and symposia. He is also named as contributing inventor on 25 patents related to polymer developments. Furthermore, he is a distinguished alumnus of UDCT (now ICT) and an adjunct professor of ICT since 2019. He was also chairman of the Indian Plastics Institute in 1992/93.

Prakash lives in Mumbai, India with his wife Varsha and they have a son, Nishith.

Preface

This work on specialty thermoplastics (STP) is one of the first of its kind and comes in an age where these materials are becoming increasingly important, not only because of their properties being superior to those of well-known engineering plastics but also because of their advantages over metals and ceramics. A notable advantage they bring over the latter is their usually lower specific gravity, which greatly helps in the reduction of part weights, which is much cherished particularly in the aerospace and automobile industries. Additionally, use of plastics makes production of articles or parts easier, with fewer steps and lower energy usage requirements.

This book covers major specialty plastics that are melt processible, in five chapters. The thermosets of comparable properties or similar applications are not covered here. As a useful working definition for specialty thermoplastics, those amorphous thermoplastics that have minimum glass-transition temperature (T_g) of 180 °C (polysulfone) and semi-crystalline thermoplastics having a minimum melting temperature (T_m) of 280 °C (polyphenylene sulfide) have been taken.

As property enhancement is constantly sought for various engineering parts, in terms of higher resistance to temperature, chemicals, flame, radiation, friction, pressure, and other external environmental factors, the usefulness of specialty thermoplastics becomes very evident. Added to their already high level of properties is the possibility for further improvement by reinforcement with various reinforcing agents such as glass fiber, carbon fiber, various metal oxides, and other additives. Specialty thermoplastics also are finding new applications as blends and alloys. Non-thermoplastics such as PTFE and PBI are also alloyed with them to give melt-processible materials.

An introduction is provided to differentiate these specialty thermoplastics from other materials, mainly engineering thermoplastics and metals and ceramics.

The specialty thermoplastics discussed here are amorphous polyaryl ether sulfones (PAES) and polyether imides (PEI), and semi-crystalline polyphenylene sulfide (PPS) and polyaryl ether ketones (PAEK). Liquid crystalline polymers (LCP) and polyaryl amides (PPA) are, however, not included here. The methods of commer-

cial manufacture of specialty thermoplastics, processing techniques, their various properties, and their main applications, of which there are myriad, are covered.

I am particularly and greatly indebted to Dr. Keki H. Gharda, Chairman and Managing Director for his strong support and guidance, which resulted in Gharda Chemicals becoming a leading STP developer and manufacturer worldwide. I am also grateful for his permission to publish, patent, and present our research works and allowing a few of the non-confidential unpublished results to be included here, along with those in the public domain.

Thanks are also due to Mr. Vincenzo Morici, former Chairman Solvay Specialty Plastics India Ltd., where I worked from 2006 to 2011, for his unflinching support for STP development in India.

I am grateful to Dr. Atul Raja for help with tables and figures as well as for reading the manuscript and giving many valuable suggestions. I am also thankful to my colleague Mr. Tushar Parida for his earlier sustained close collaboration in the development work on various specialty thermoplastics with me. Thanks are also due to Dr. Aditi Kapadia, Dr. Harishchandra Natu, Mr. Ashok Chavan, Ms. Foram Prajapati, Mr. Pragnesh Damania, Mr. Husaini Bookwala, Mr. Anith Vijayan, Dr. Mathew Abraham, Mr. Amit Kundu, Mr. Sanjay Limaye, Dr. Praveen Karandikar, and many others who worked with me at Gharda Chemicals for the development of various STPs. I am also indebted to Mr. Jaimin Zaveri, Mr. Ralph Lavi, and Mr. Bernard Lanham for various discussions on applications and commercialization of STPs. I am indebted to Mr. Satish Limaye, the IP manager at Gharda Chemicals, for his help with patents and literature references covered here.

I joined the Department of Polymer Science at the University of Akron in January 1970 and in September of that year I signed with Prof. Dr. J.P. Kennedy for my thesis work. I completed my research on isobutylene cationic polymerization by the end of 1974. Little did I know then that I would have the chance to work on electrophilic polymerization some years later on, and that also for developing specialty thermoplastics. I am grateful to Prof. Kennedy not only for getting me initiated into this wonderful chemistry but also for getting me started in industrial polymerizations, patenting, and publications to boot.

This book would not have been possible without strong support of Dr. Mark Smith for the last three years. I am deeply indebted to him and Dr. Julia Diaz-Luque of Hanser Publications for their full encouragement, tremendous editorial support, and much patience to see this book through.

I am also obliged to various corporations and trade and scientific magazines for granting permission to include their particular references in the text.

Finally, I am indebted to my wife Varsha and other family members for sparing many a moment ungrudgingly to allow me to work of this book.

Contents

Dedication	V
The Author	VII
Preface	IX
1 Introduction	1
1.1 Technical Requirements	2
1.2 Production	3
1.3 Processing of STP	5
1.3.1 Powder Processing	5
1.3.1.1 Compression Molding	6
1.3.1.2 Powder Extrusion for Compounding	6
1.3.2 Processing of STP Granules	10
1.4 Properties of STP	11
1.5 Marketing	18
1.6 Performance	18
2 Polyaryl Ether Sulfones (PAES)	21
2.1 Introduction	21
2.2 Preparations and Production	25
2.2.1 Nucleophilic Polymerization	25
2.2.2 Electrophilic Polymerization	28
2.2.3 Production of Polysulfones	29
2.2.4 Resin Powder Processing	32
2.2.4.1 Membrane Preparation	33

2.2.4.2	Powder Coatings	34
2.2.4.3	Compounding	37
2.2.5	Processing of PAES Compounds	38
2.2.5.1	Extrusion	39
2.2.5.2	Injection Molding	39
2.2.5.3	Miscellaneous Processing	40
2.2.6	PAES Properties	41
2.2.6.1	Optical and Chemical Properties	41
2.2.6.2	Thermal Properties	44
2.2.6.3	Mechanical Properties	47
2.2.6.4	Thermomechanical Properties	57
2.2.6.5	Rheological Properties	61
2.2.6.6	Electrical Properties	63
2.2.7	PAES Recycling	63
2.2.8	PAES Performance and Applications	65
2.2.8.1	Food and Medical Applications	66
2.2.8.2	Plumbing Applications	70
2.2.8.3	Electrical and Electronic Applications	71
2.3	Summary	74
3	Polyetherimides (PEI)	77
3.1	Introduction	77
3.2	PEI Preparations	79
3.2.1	PEI by Etherification	79
3.2.2	PEI by Imidation	81
3.3	PEI Production	84
3.4	PEI Processing, Properties, and Performance	86
3.4.1	PEI Processing	86
3.4.1.1	Powder Processing	86
3.4.1.2	Compounding	87
3.4.2	PEI Granules Processing	87
3.4.2.1	Extrusion	87
3.4.2.2	Additive Manufacturing/3D Printing	89
3.4.2.3	Fiber Spinning	92

3.4.2.4	Film	93
3.4.2.5	Injection Molding	93
3.4.3	PEI Properties	94
3.4.3.1	Thermal Properties	101
3.4.3.2	Thermomechanical Properties	102
3.4.3.3	Rheological Properties	104
3.4.3.4	Miscellaneous Properties	105
3.4.4	PEI Performance and Applications	106
3.4.4.1	Automobile Applications	107
3.4.4.2	Aerospace Applications	109
3.4.4.3	Food and Medical Applications	110
3.4.4.4	Electrical Applications	112
3.4.4.5	Miscellaneous Applications	112
3.5	Summary	112
4	Polyphenylene Sulfide (PPS)	115
4.1	Introduction	115
4.2	Preparation	116
4.2.1	PPS Reaction Mechanism	118
4.2.2	PPS Production	120
4.3	PPS Processing, Properties, and Performance	121
4.3.1	Powder Processing	122
4.3.2	Resin Curing	122
4.3.3	Coating	125
4.3.4	Compression Molding	128
4.3.5	3D Printing	128
4.3.6	Compounding	128
4.3.7	PPS Compounds Processing	129
4.3.7.1	Injection Molding	129
4.3.7.2	Fiber Spinning	132
4.3.7.3	Extrusion of Stock Shapes	133
4.3.8	PPS Properties and Performance	133
4.3.8.1	Crystallinity	134
4.3.8.2	Thermal Properties	135

4.3.8.3	Thermomechanical Properties	136
4.3.8.4	PPSMechanical Properties	138
4.3.8.5	Rheological Properties	139
4.3.9	PPS Performance and Applications	140
4.3.9.1	Automobile Applications	141
4.3.9.2	Electrical Applications	143
4.3.9.3	General Engineering Applications	143
4.4	Summary	144
5	Polyaryl Ether Ketones (PAEK)	147
5.1	Introduction	147
5.2	Preparation of PAEK	153
5.2.1	PAEK Nucleophilic Polymerization	153
5.2.2	PAEK Electrophilic Polymerization	154
5.3	Production of PAEK	156
5.3.1	PEEK Production	156
5.3.1.1	PEEK Nucleophilic Chemistry	156
5.3.1.2	PEEK Electrophilic Chemistry	157
5.3.2	PEK Production	158
5.3.2.1	PEK Nucleophilic Chemistry	158
5.3.2.2	PEK Electrophilic Chemistry	159
5.3.3	PEEKK Production	160
5.3.3.1	PEEKK Nucleophilic Chemistry	160
5.3.3.2	PEEKK Electrophilic Chemistry	160
5.3.4	PEKEKK Production	161
5.3.4.1	PEKEKK Nucleophilic Chemistry	161
5.3.4.2	PEKEKK Electrophilic Chemistry	161
5.3.5	PEKK Production	162
5.3.5.1	PEKK Electrophilic Chemistry	163
5.3.5.2	PEKK Nucleophilic Chemistry	165
5.3.6	Modified PAEK	167
5.3.6.1	Sulfonated PAEK	167
5.3.6.2	PAEK Copolymers	170

5.4	PAEK Blends and Alloys	170
5.4.1	PEEK/PEK Blends	171
5.4.2	PAEK/PBI Blends	172
5.4.3	PAEK/PTFE Blends	178
5.5	PAEK Processing, Properties, and Performance	182
5.5.1	PAEK Resin Processing	182
5.5.1.1	Coatings	182
5.5.1.2	Compression Molding	183
5.5.1.3	Compounding	185
5.5.1.4	3D Printing by Laser Sintering	186
5.5.2	PAEK Granules Processing	189
5.5.2.1	Extrusion of Stock Shapes	189
5.5.2.2	PAEK Injection Molding	191
5.6	PAEK Properties	193
5.6.1	PAEK Thermal Properties	193
5.6.2	PAEK Thermo-Mechanical Properties	199
5.6.3	PAEK Mechanical Properties	205
5.6.4	PAEK Rheological Properties	208
5.6.5	PAEK Flame Resistance Properties	211
5.6.6	PAEK Electrical Properties	213
5.6.7	PAEK Crystallization Properties	214
5.6.8	PAEK Radiation Resistance	215
5.6.9	PAEK Recycling	216
5.7	PAEK Performance and Applications	217
5.7.1	General Engineering	218
5.7.2	Medical Applications	224
5.7.3	Auto Applications	225
5.7.4	Composites	225
5.7.5	Miscellaneous Applications	226
5.8	Summary	226
	Index	231

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.

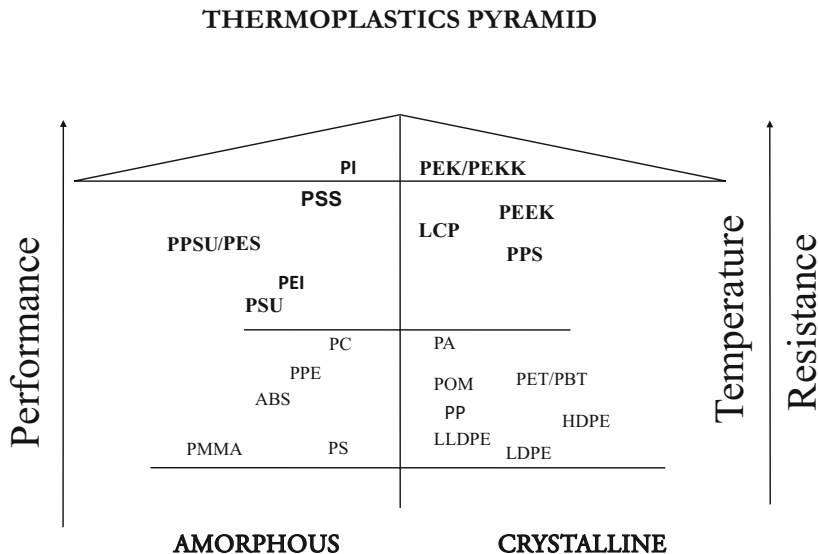


Figure 1.1 STPs positions in plastics pyramid

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 $-\text{SO}_2-$ and $-\text{O}-$ 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 $-\text{S}-$ in PPS and the near steric equivalence of $-\text{O}-$ and $-\text{CO}-$ 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 $-\text{O}-$, $-\text{S}-$, $-\text{CO}-$, $-\text{SO}_2-$, $-\text{C}(\text{Me})_2-$, $-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-$, or $(-\text{CO})_2\text{N}-$. 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 $0\text{ }^\circ\text{C}$ to $75\text{ }^\circ\text{C}$ for PEKK, to less than $200\text{ }^\circ\text{C}$ to $220\text{ }^\circ\text{C}$ for PEI and PAES, to near $270\text{ }^\circ\text{C}$ for PPS, and to as high as $320\text{ }^\circ\text{C}$ 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.