3. Morphology

3.1 Introduction

The morphology of polymers, as defined in the Encyclopedia of Polymer Science and Engineering [76], is concerned with the shape, arrangement and function of crystals alone or embedded in the solid. Polymers are either homogeneous amorphous or heterogeneous semi-crystalline [76, 77, 168]. Amorphous thermoplastics do not contain crystalline structures while semi-crystalline thermoplastics are characterized by the presence of ordered crystalline regions as well as amorphous regions. The term crystalline polymer always implies partially crystalline. The degree of crystallinity may be as high as 60-65% in some cases [77].

The influence of morphology on the properties of composites is a major issue with semi-crystalline thermoplastic based composites. A great deal of research has been devoted in studying morphology-processing and morphology-property relationships with PEEK and PPS matrices and their composites [58, 106 - 113, 130, 135, 169 - 173]. In this section, the factors influencing the morphology of semi-crystalline thermoplastics such as processing conditions and the presence of fibres, as well as the interrelationships between morphology and properties are presented.

3.2 Factors Influencing Morphology of Semi-Crystalline Thermoplastics

3.2.1 Processing Conditions

Many factors can influence the morphology of semi-crystalline thermoplastics including copolymer(s), molecular weight, presence of other materials (nucleating agents, impurities, fibres, etc.) and processing conditions (temperature at melt and the time it is held at this temperature, cool-down rate, etc.) [170]. An irregular chemical structure such as chain branching may prevent the formation of ordered regions [92]. But in other cases, crystallization may be impeded for kinetic reasons despite a regular chemical structure of the chain molecules. For example, the normal recommended cooling rates to achieve optimum composite properties with PEEK matrix are between 10 and 700° C/ minute [111, 174]. In this range, there is little variation in the degree of crystallinity (25 to 30%). At cooling rates lower than 10° C/ min, degrees of crystallinity in excess of 35% will be achieved which will result in some reduction in toughness. At cooling rates greater than 700° C/minute, growth of spherulites (crystalline texture of melting crystallized polymer [173]) will be incomplete and the optimum level of crystallinity will not be reached and some reduction in stiffness and resistance to hostile solvents may result. At a cooling rate greater than 2000° C/minute, PEEK matrix will be essentially amorphous. However, a satisfactory degree of crystallinity can still be attained by a second stage of post-annealing in the range of 200-300° C for about 20 minutes to achieve the optimum level of crystallinity and performance [174]. Figure 13 shows the

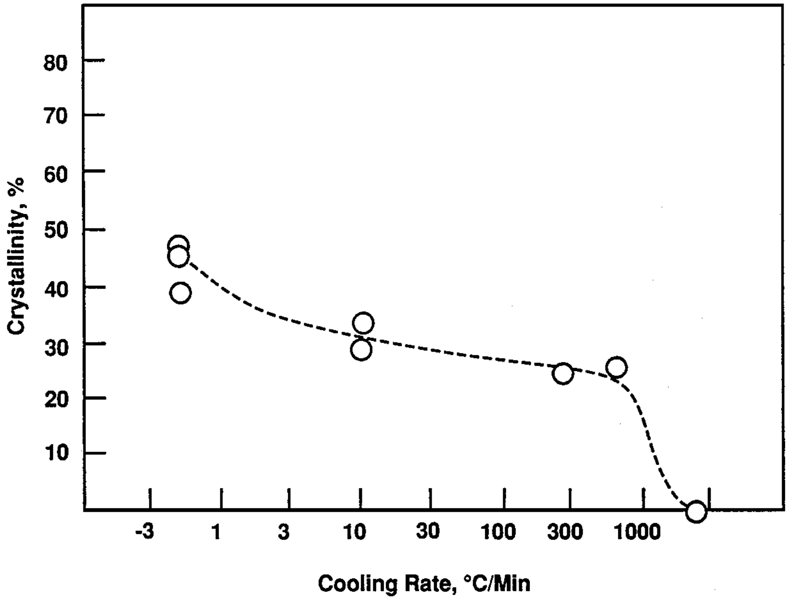

FIGURE 13. Degree of Crystallinity of PEEK as a Function of Cooling Rate [111]

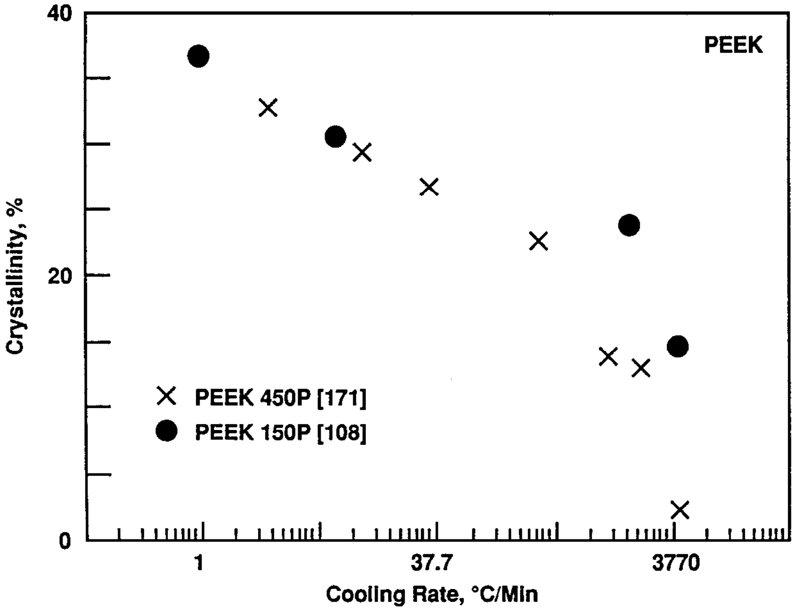

FIGURE 14. Degree of Crystallinity of PEEK as a Function of Cooling Rate [108]

degree of crystallinity of neat PEEK resin as a function of cooling rate obtained by Blundell et al. [111] while Figure 14 presents results obtained by Talbott et al. [108] and Velisaris and Seferis [171]. A high cooling rate leads to lower crystalline contents in the final product. Successful models have been developed which estimate the degree of crystallinity of a semi-crystalline thermoplastic composite from a known cooling history [107, 112].

Processing cycles not only affect the degree of crystallinity but also the spherulite size [1, 135, 175]. Table 17 shows the effect of cooling rate on spherulite size of PEEK resin. A low cooling rate results in the formation of large spherulites while smaller spherulites can be formed by fast cooling. The same observations have been made for PPS resin [135]. It was also found that by annealing amorphous PPS above Tg (95° C), small crystallites can then be formed [135].

Crystallinity is also influenced by other processing parameters such as the temperature to which the polymer is heated and the time it is held there [100, 130, 135, 172, 173]. A temperature high enough to melt all the crystalline material formed during previous thermal treatments has to be chosen when processing semi-crystalline thermoplastics [58, 112]. This ensures a completely amorphous structure and allows the obtention of the desired microstructure and degree of crystallinity in a subsequent processing from the melt. For PEEK, melting at 360° C for 2 min and even at 380° C (for a shorter time) will leave crystalline remnants [112]; and therefore a temperature of 400° C is rather recommended to ensure all crystalline material is melted.

Beever et al. [135] found that varying the total residence time of the carbon/ PPS composite in the mold from 7 to 20 minutes and varying the molding temperature from 291 to 360° C had no effect on mechanical properties. However, Ma et al. [130] have reported that for PPS long heating times lead to lower ultimate crystallinity and may alter the molecular structure, mechanical properties and thermal stability. Table 18 presents the degree of crystallinity of PEEK versus the holding temperature at melt obtained by Xiao and Hoa [173]. Higher melt temperature leads to lower crystallinity. As mentioned by these authors, this might be of a great concern during a repair process using welding techniques. Heating is localized at the damage area while the surrounding areas are subjected to lower melting temperatures resulting in undesired changes in degree of crystallinity and then mechanical properties in those surrounding areas. Figure 15 shows the degree of crystallinity of PEEK as a function of total melt annealing time at 396° C obtained by Lee and Porter [110]. Included in this figure are neat PEEK resin and carbon fibre reinforced PEEK that have undergone different molding conditions (pre-heating times of 30 and 100 minutes and cooling rates of 0.6 and 7° C/minute). In all cases, the degree of crystallinity decreased with increased total melt-annealing time. Crystallization on the carbon fibre tends to occur with carbon fibre reinforced

TABLE 17. Effect of Processing Cycle on Spherulite Size [1]

Process Cycle	Effect on PEEK Morphology	Effect on Composite Mechanical Performance
Quench	Low percent crystallinity	Tough, but lower matrix modulus equals reduced compression strength
Slow cool to nonoptimum crystallization temperature	Large spherulites	Decreased toughness
Fast cool to optimum crystallization temperature	Small spherulites	Increased fracture toughness

TABLE 18. Effect of Holding Temperature at Melting on the Degree of Crystallinity [173]

holding temperature	degree of crystallinity by WAXS	by DSC
400°C	0.26	0.26
370°C	0.24	0.27
350°C	0.29	0.28
340°C	0.33	0.21
335°C	0.35	-

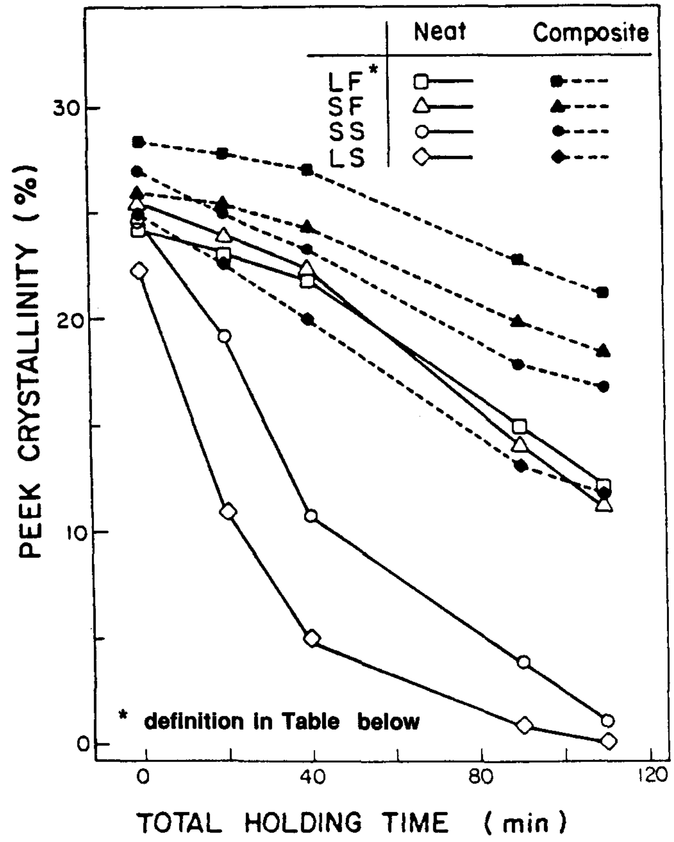

FIGURE 15. Crystallinity at 306°C in 7 min versus Total Melt-annealing Time at 396°C for Neat PEEK and Carbon Reinforced PEEK [110]

Compression Molding Condition of PEEK and Carbon Reinforced PEEK

Sample[a] Code	Preheating Time[b] (min)	Cooling Rate (°C/min)
SF	30	−7
SS	30	−0.6
LF	100	−7
LS	100	−0.6

[a] The first letter of sample code stands for preheating time: S (short) for 30 min and L (long) for 100 min. The second letter stands for cooling rate: F (fast) at −7°C/min and S (slow) at −0.6°C/min.

[b] At 390°C without pressure followed by compression molded at 390°C and 2 MPa for 30 min.

PEEK which has been preheated in the melt for 100 minutes. Correspondingly, as explained later (Foreign Surfaces, section 3.2.2), these composites have shown about twice the transverse tensile strength and strain-to-failure of those preheated for only 30 minutes.

The degree of crystallinity may also vary through the thickness of a laminate [1, 108, 109]. Incomplete or non-uniform crystallization may take place if, for example, a thick sheet of APC-2 in the molten state is transfered to a cold metal mold with good thermal transfer from the APC-2 sheet [109]. Thin sheets in this case can be totally amorphous. Blundell and Willmouth [109] have presented a simple heat flow model enabling predictions of the temperature profile through the thickness of APC-2 sheets based on time after transfer from the melt state to a moulding tool held at a fixed temperature.

3.2.2 Foreign Surfaces

The morphology of a polymer is affected by the presence of foreign surfaces [100, 110, 112, 113]. PEEK was found to crystallize at higher temperatures with higher nucleation densities as the fibre content of a carbon reinforced composite was increased [100, 110]. The fibre surfaces act as nucleating sites. Typical crystalline content of PEEK in a 50% carbon fibre composite is 35% as measured by DSC [100]. Blundell et al. [106] divide nucleation sites in carbon/PEEK composites into three types: nucleation from contact points between fibres or regions where the fibres are almost in contact (Figure 16), nucleation from within the matrix (Figure 17) and nucleation at a free fibre-polymer interface (Figure 17). The relative abundance of each type of nucleation depends on the circumstances. Crystallization at lower temperatures for example encourages matrix nucleation [106, 111] while longer melt holding times favour crystallization on the carbon surfaces [110]. They also observed that the nucleation from a free fibre-matrix surface is relatively rare, at least not common enough to give the appearance of a "trans-crystalline" layer. However, transcrystallinity, described as the columnar growth of crystals perpendicular to the fibre surface has been observed by other researchers [100, 110, 123, 169]. It has been associated with the improvement of the interfacial bond between PEEK and the fibres resulting in better mechanical properties [100, 110]. But Blundell et al. [106] state that "the reported transcrystallinity effects sometimes seen from fibers embedded in thin PEEK films are related to the fiber-fiber contact sites in APC-2 and occurs where the carbon fiber comes into close contact with the glass slides sandwiching the film". Turner and Cogswell [169] have explored the varying interfacial properties that result from the differing fibre types used in PEEK based composites. Fibre types include E,R and S glass fibres, aramid fibres, and high strength (HS), high modulus (HM), intermediate modulus (IM) and ultra-high modulus (UHM) carbon fibres. All laminates were prepared using the same procedures recommended for APC-2. With all types of fibres, there was a high incidence of spherulitic nuclei associated with two closely adjacent or touching fibres. They believe that this is probably due to the thermal contraction of the resin phase during cooling and the local geometry which together produce a stress concentration at such fibre contact points inducing

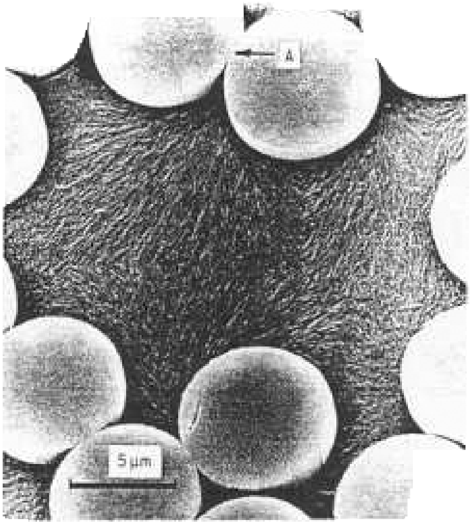

FIGURE 16. Scanning Electron Micrograph of Etched Transverse Section of a Standard Laminate That Has Been Slowly Cooled from the Melt. "A" Indicates a Typical Nucleation Event at a Fibre-Fibre Contact Point [106]

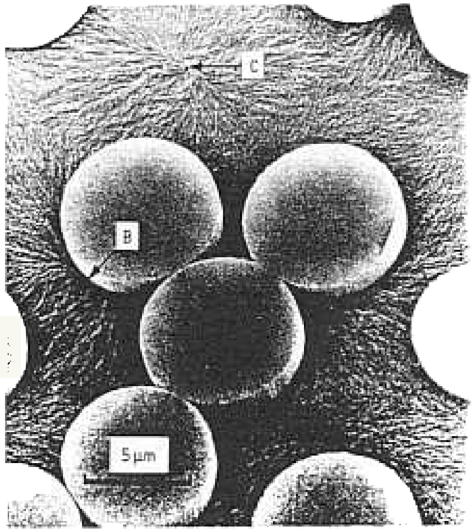

FIGURE 17. Scanning Electron Micrograph of Etched Transverse Section of a Standard Laminate That Has Been Slowly Cooled from the Melt. "B" Indicates Nucleation from a Fibre Surface and "C" Indicates Nucleation from within the Matrix [106]

nucleation. In all cases involving carbon fibres reinforcement, initiation of spherulitic growth from the fibre surfaces was also apparent in matrix morphology. The on-fibre nucleation indicates that fibre and resin are in close contact but as Turner and Cogswell [169] suggested this does not imply that good bonding is guaranteed, although it is a necessary condition for good bonding.

3.3 Morphology-Property Relationships of Semi-Crystalline Thermoplastics

It is well recognized that the mechanical properties of semi-crystalline thermoplastics depend on their morphology [1, 58, 77, 107, 108, 135, 175]. The degree of crystallinity, the number and size of spherulites, the crystalline structure and the crystalline orientation affect the properties of semi-crystalline polymers [135]. Orientation can be responsible for anisotropy in the mechanical properties. Larger spherulites are inherently stiffer but less ductile (Table 17). As in cross-linking, crystallization can enhance stiffness and Tg by constraining molecular mobility [75]. Figure 18 shows toughness and tensile strength properties of neat PEEK resin as a function of the degree of crystallinity. In general, a lower level of crystallinity will produce higher elongation and better toughness but with the trade-off of lower strength, thermal stability and chemical resistance. Diffusion of the solvents into a semi-crystalline thermoplastic is more difficult than with an amorphous thermoplastic due to the densely packed spherulites in the crystalline region [1, 77]. Available results on the effects of morphology on the properties of PEEK and PPS based composites are presented below.

PEEK: Talbott et al. [107, 108] have evaluated the tensile, compressive and shear properties, as well as fracture toughness of the neat resin PEEK 150P having degrees of crystallinity ranging from 15 to 40% and having different processing histories. The results which they have obtained are shown in Figures 18 to 22. The strength and stiffness in both tension and shear increase with crystalline content but compression strength remains relatively unaffected. However, due to the highly non-linear behavior of the material during compression, these data must be interpreted with caution. As shown in Figures 18 and 22, the decrease in toughness with increasing degree of crystallinity is significant. Talbott et al. [108] also measured mode I and mode II fracture energies for carbon reinforced PEEK (APC-2) for the crystalline content range of 0 to 33%. Results are presented in Figure 23 where fracture energies decrease significantly with increasing crystalline content. These authors also concluded that the data they have obtained suggest that the values of the tensile and compressive properties of the polymer seem to be sensitive to processing history; e.g. specimens having the same degree of crystallinity but having a different processing history may result in different tensile and compressive properties. However, within the range studied, the shear strengths and moduli of the polymer seem to be insensitive to the thermal history employed during processing and depend mainly on the degree of crystallinity. In the case of fracture energy, cooling only or cooling and reheating resulted in nearly the same fracture energy as long as the crystalline content after processing was the same as before.

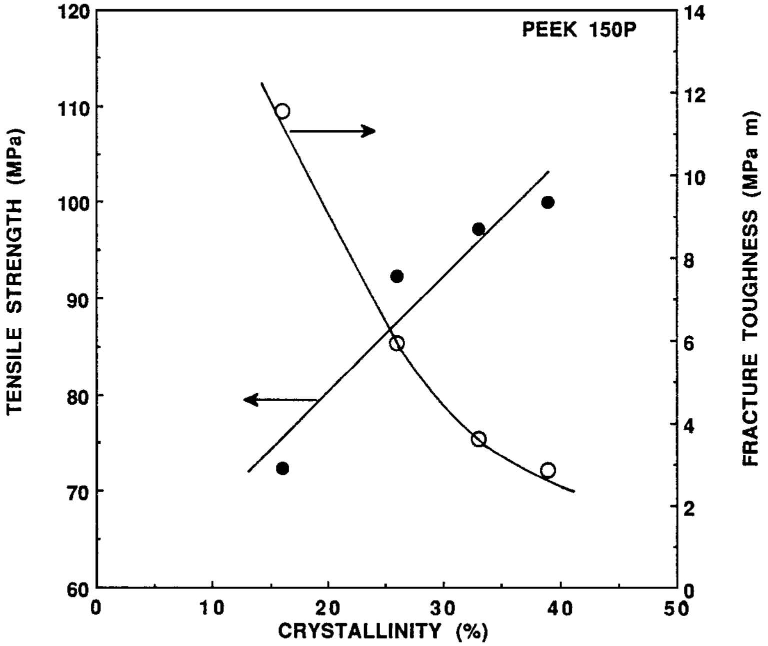

FIGURE 18. Tensile Strength and Fracture Toughness of PEEK Neat Resin as a Function of Degree of Crystallinity [108]

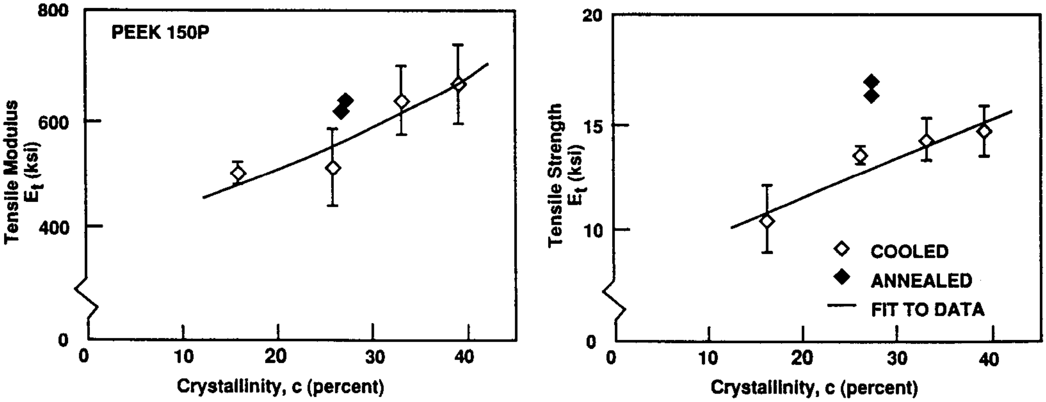

FIGURE 19. Tensile Properties of PEEK 150P as a function of Degree of Crystallinity [108]

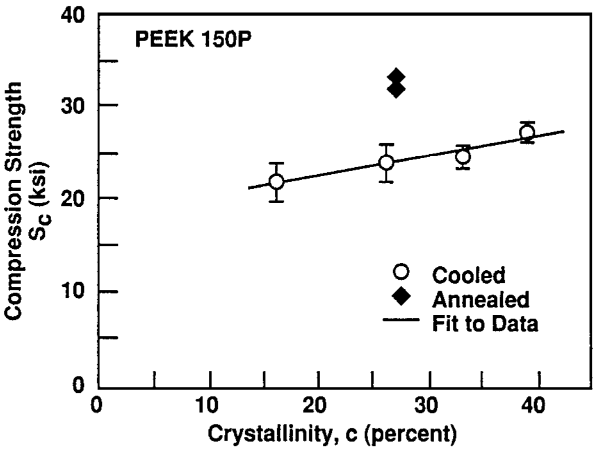

FIGURE 20. Compression Strength of PEEK 150P as a Function of Degree of Crystallinity [108]

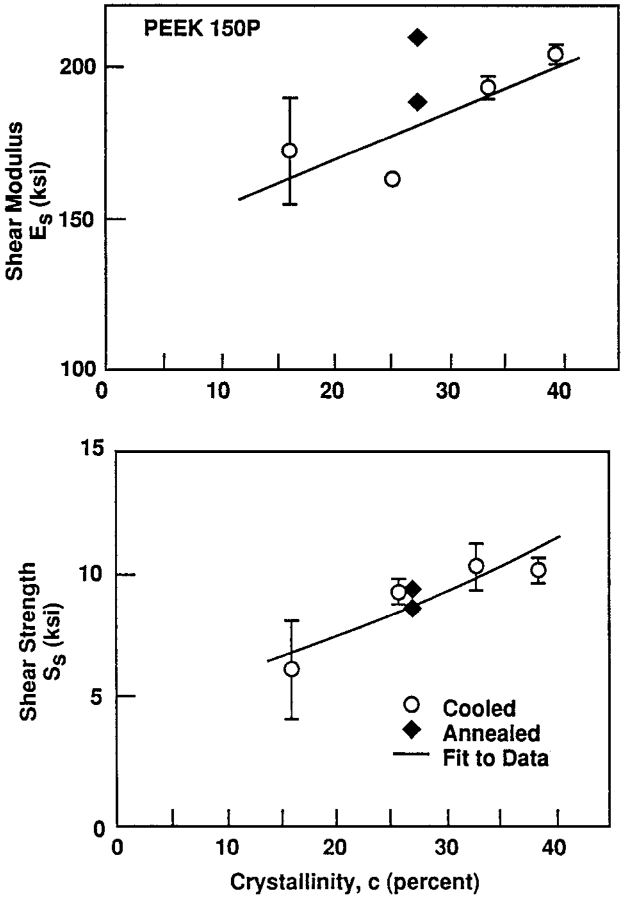

FIGURE 21. Shear Properties of PEEK 150P as a Function of Degree of Crystallinity [108]

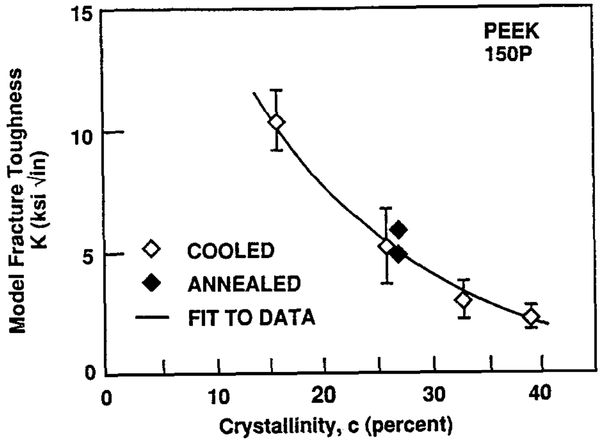

FIGURE 22. Measured Mode I Fracture Toughness of PEEK 150P as a Function of Degree of Crystallinity [108]

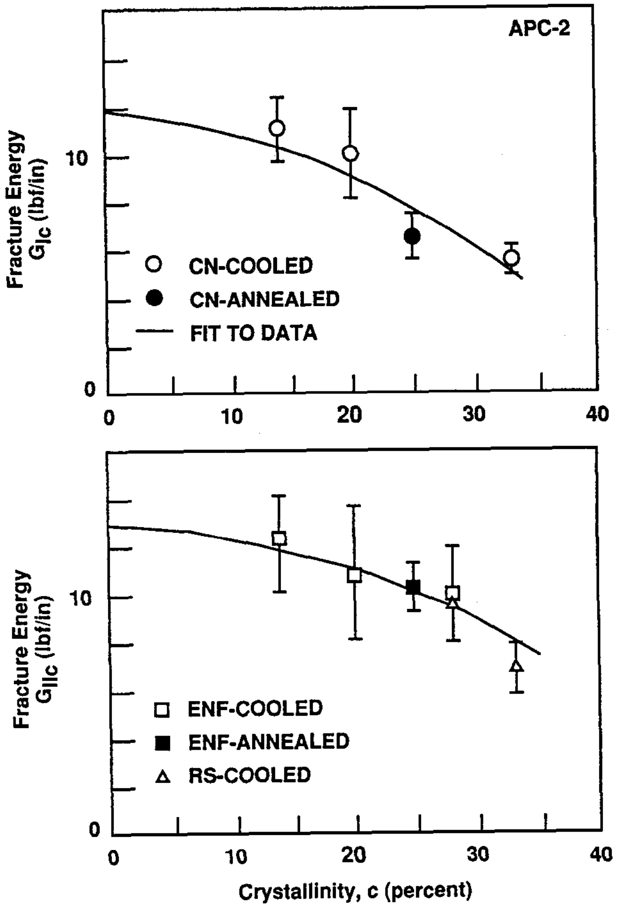

FIGURE 23. Mode I and Mode II Fracture Energy of APC-2 as a Function of Degree of Crystallinity [108]

Cebe et al. [58] have studied mechanical properties and morphology of samples of PEEK having different thermal histories. They found that the degree of crystallinity is not as important as processing history when determining room temperature mechanical properties. Samples with the same degree of crystallinity had very different tensile properties, depending on rate of cooling from the melt. This was attributed to differences in crystal size and to size distribution.

PPS: The effect of moulding parameters such as temperature, pressure, total residence time at melt temperature and cooling rate on mechanical properties of neat PPS resin and carbon/PPS composites have been investigated by Beever et al. [135]. Table 19 shows the effects of thermal history on the mechanical properties of the neat resin. The effects of annealing on the mechanical properties of carbon/PPS composites are shown in Table 20. In general, the differences are not very large except for the compressive properties. The unannealed amorphous matrix is softer allowing the fibres to buckle under compression resulting in low compressive strength values. After annealing, the matrix is stiffer and the compressive strengths are also significantly higher. Longitudinal tensile and flexural strength are somewhat higher for annealed specimens but the fracture toughness is lower than that of the amorphous material. Davies et al. [136] also found in their study on delamination behavior of carbon reinforced PPS that the effect of annealing reduces slightly the toughness values in mode I and II (from 0.9 to 0.8 kJ/m^2 in both cases); the degree of crystallinity being increased in the case of annealed specimens (about from 5 to 30%) (Table 21). G_{Ic} and G_{IIc} toughnesses for PPS were compared to two epoxy based composites, T300/914 and IM6/6376, and were found to be significantly higher than those for the epoxy materials.

3.4 Summary

This brief review concerning morphology of semi-crystalline polymers primarily shows that polymer morphology is a fundamental issue with semi-crystalline polymers. It is important to know how the morphology of the matrix of the composite of interest is affected by processing conditions and how mechanical properties are affected by the morphology of the polymer. If, for example, toughness is highly desired for a particular application, a low level of crystallinity would be preferred and may be achieved by proper processing conditions. But one has to be careful that the low degree of crystallinity material in service will not be subsequently exposed to annealing temperatures for a long time thus increasing its crystalline content and most likely decreasing its toughness. In addition, special attention has to be paid to non-uniform heating during processing semi-crystalline thermoplastic based composites especially in the cases of thick and tapered laminates or during a repair process using welding techniques. Polymer morphology such as degree of crystallinity may vary through the thickness of thick and tapered laminates or in the vicinity of the damaged area in the case of repair resulting in undesired changes in mechanical properties.

TABLE 19. Effect of Thermal History on Mechanical Properties of Unoriented PPS Film [135]

Molding Condition	Quick Quenched [1]	Quick Quenched [2]	Slow Cooled
Annealed at 200°C	no	yes	no
Density, g/cm^3	1.309	1.346	1.351
% crystallinity [a]	0	32	37
Tensile modulus, MPa	1926	2574	2709
Tensile break, MPa	44.5	80.7	51.3
Elongation at break, %	20.0	4.8	3.4
Tensile yield, MPa	63.6	...	...
Elongation at yield, %	5.0	...	...

[a] ρ_a = 1.31 g/cm^3 = density of 100% amorphous PPS.
ρ_c = 1.43 g/cm^3 = theoretical density of 100% crystalline PPS (from unit cell parameters).

[1] **unannealed**

[2] **annealed at 200°C**

TABLE 20. Effect of Annealing on Mechanical Properties of Ryton-PPS/Carbon Fiber[a] Unidirectional Laminates [135]

Property	Morphology	
	Unannealed [1]	Annealed [2]
Longitudinal tensile modulus, GPa (Msi)	131 (19.0)	135 (19.6)
Longitudinal tensile strength, MPa (ksi)	1490 (216)	1641 (238)
Transverse tensile modulus, GPa (Msi)	9.0 (1.3)	9.0 (1.3)
Transverse tensile strength, MPa (ksi)	36.6 (5.3)	31.7 (4.6)
Longitudinal flexural modulus, GPa (Msi)	118 (17.1)	121 (17.6)
Longitudinal flexural strength, MPa (ksi)	1083 (157)	1290 (187)
Transverse flexural modulus, GPa (Msi)	7.6 (1.1)	9.0 (1.3)
Transverse flexural strength, MPa (ksi)	56.6 (8.2)	53.1 (7.7)
Longitudinal compressive strength, MPa (ksi)	338 (49)	559 (81)
Transverse compressive strength, MPa (ksi)	103 (15)	124 (18)
Short beam shear strength, MPa (ksi)	69 (10)	...
G_{Ic}, kJ/m^2 (in. · lb/in.^{2})	0.8 (4.4)	0.6 (3.4)[b]

[a] **Prepreg contains 68±2% by weight carbon fiber.**

[b] **Values as high as 1.3 kJ/m^2 (7.8 in.·lb/in.^{2}) have been obtained by film stacking.**

[1] **Quenched specimens in the amorphous state.**

[2] **~35% degree of crystallinity, annealed after quenching.**

TABLE 21a. Mode I Results, Values of G_{Ic} [136]

SPECIMEN TYPE			DEGREE OF CRYSTALLINITY (%)	COMPLIANCE METHOD (J/m^2)	AREAS METHOD (J/m^2)
C/PPS	Thin (3mm)	As rec	5	-	918
C/PPS	Thin	Annealed	30	-	799
C/Epoxy	Thin (4mm)	T300/914	-	124	137
C/Epoxy	Thin	IM6/6376	-	182	633
C/PPS	Thick (20 mm)	As rec	22	196	818
C/PPS	Thick	Annealed	31	152	756
C/Epoxy	Thick	T300/914	-	185	151

TABLE 21b. Results from ENF Tests [136]

SPECIMEN TYPE		DEGREE OF CRYSTALLINITY (%)	G_{IIc} (J/m^2)
C/PPS	As rec	5	933
C/PPS	Annealed	30	802
C/Epoxy	T300/914	-	518
C/Epoxy	IM6/6376	-	658