

Emerging Trends in Polymer Matrix Composites

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ABSTRACT

The performance characteristics of PMC products are determined by the microstructure developed during the processing of composite materials. The structure development in processing is the result of interaction of process parameters and inherent material characteristics. The properties of PMCs can thus be manipulated through both changes in the materials composition and process conditions. The present article illustrates the scientific approach followed in engineering of matrix materials and optimization of the processing conditions with specific reference to case studies on toughening of thermosetting resins and structure development in injection molding of thermoplastic composites.

A novel approach is demonstrated for toughening of unsaturated polyester resins that involves the use of reactive liquid polymers chemically bonded to the matrix. The use of processing science is demonstrated by the significant effect of the mold temperature on the crystallinity and properties of molded poly (phenylene sulfide), a high performance engineering thermoplastic. An interactive approach is proposed for specific product and applications development.

1. INTRODUCTION

Polymers and composites are increasingly replacing conventional materials in engineering applications. Engineering applications are normally those wherein a material is subjected to extreme static or dynamic mechanical loading in a high temperature and chemically severe environment, sometimes on a continuous basis. Thus a combination of chemical, thermal, mechanical and/or electrical properties is required of the material. Typical examples of such applications would be gears, bearings, pulleys, pressure pipes, pump impellers, valve seats, seals, auto bumpers and fenders, radiator fan blades and covers, etc. The composites use polymers as the matrix for the reinforcing fibres/fillers. For example, fiberglass reinforced epoxy suspension springs have been successfully tested for light commercial vehicles; metal pipes are being replaced by filament wound FRP pipes in oil exploration; bullet-proof vests can now be prepared from man-made lightweight aramid fibres;

carbon fibre reinforced epoxy composites are used in structural components of an aeroplane such as taileron; and composite ropes made of aramid and polypropylene filaments are used in mining ocean floors where steel wires fail. Polymer matrix composites (PMCs) are thus a versatile class of materials offering a broad range of properties¹.

1.1 Perspective

High performance PMCs have moved out of the materials laboratories into the 'real world'. The prototype products in transportation include low pollution commuter cars, mobile office vans, railway container cars, two-passenger hovercrafts and executive commuter planes. The advent of such structurally engineered composite products has been the result of an 'integrated development approach' linking the development and synthesis of materials with the design and processing of their final products. The new materials paradigm strives to translate the knowledge

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of materials behaviour into the much broader arena of manufacturing systems, swiftly and efficiently. The prerequisite for implementing such an approach is a sound scientific understanding of the processing-microstructure-properties continuum in PMCs.

The emerging trends in materials technology, processing science and performance testing of composites pertain to the following aspects:

- (a) High strength, high modulus fibres from conventional polymers like high density polyethylene (HDPE),
- (b) Reinforcing fibres from liquid crystal polymers,
- (c) Toughening of thermosetting and thermoplastic matrix resins,
- (d) Innovative composites processing technologies such as hot press forming of fibre reinforced thermoplastic mats, thermoplastic pultrusion, and drapeable thermoplastic fibre preforms,
- (e) Structure development in net shape forming processes (injection molding, extrusion, spinning) for controlling micro-structure,
- (f) Process design through computer modelling/simulation,
- (g) Computer aided design of composite structures and products,
- (h) Bonding, jointing and fastening,
- (i) Non-destructive techniques for structural evaluation,
- (j) Environmental degradation and damage tolerance of composites, and
- (k) Maintenance, repair and recycle of composites.

In the present paper, the scientific approach followed in materials and processing technology development is illustrated with reference to specific case studies in toughening of thermosetting matrix materials and structure development in injection molding thermoplastic composites.

2. MATERIALS INNOVATIONS

The PMCs are made from thermosetting or thermoplastic matrix materials, reinforced with high strength/high modulus fibres. Besides the reinforcing fibres, a variety of fillers can also be used for modifying the properties. These include mica, talc, wollastonite etc. As a result of such a large number of degrees of

freedom available to the materials engineers, it is possible to tailor make composites over a broad property spectrum to suit specific performance and cost targets. The total consumption of PMCs reached a level of about 2 million tonnes worldwide in 1989. The major reasons for the increasing use of composites include their light weight, corrosion resistance, design flexibility and ease of processibility.

2.1 Thermoplastics

In recent years, thermoplastic matrix materials are increasingly used because of their considerable ease of processing relative to thermosets, and their amenability to recycling. The thermoplastic materials used in composites are speciality polymers with high thermal and mechanical performance levels. These are termed 'engineering plastics' and they can be categorised into semicrystalline and amorphous polymers as summarised in the Tables 1 and 2. In the case of the crystalline polymers, the heat distortion temperature of the material lies in between the glass transition temperature and melting point, whereas for amorphous thermoplastics, the heat distortion temperature is comparable to the glass transition temperature. The thermal properties of the thermoplastic matrix materials thus determine the maximum permissible temperature for using the composites. Out of the various thermoplastics, polyphenylene sulfide, polyether-ether-ketone and polyether sulfones are the preferred matrix materials for high performance composites based on carbon fibres. All the engineering thermoplastics can be readily compounded with chopped glass fibres to give FRTP pellets for subsequent processing by injection molding. The representative properties of selected thermoplastic matrix materials are summarised in Table 3.

In the past 10 years, a new class of polymers termed 'liquid crystal polymers' (LCP) have emerged for engineering and structural applications. These polymers are also described as 'molecular composites' and they offer properties comparable to fibre reinforced polymer composites, without the addition of fibres. The chemical structure of the LCPs consists of rigid chain segments that act as molecular scale fibre reinforcement, and flexible chain segments constituting the matrix phase. Since these two types of chain segments are connected by very strong covalent bonds, the LCPs offer properties comparable to composites in a homogeneous system.

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Table 1. Semicrystalline engineering plastics

Material	Molecular formula	Glass transition temperature (°C)	Melting temperature (°C)
Nylon 6	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C} - (\text{CH}_2)_5 - \text{NH} - \end{array}$	35	225
Poly(butylene terephthalate)	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ -\text{C} - \text{C}_6\text{H}_4 - \text{C} - \text{O} - (\text{CH}_2)_4 - \text{O} \end{array}$	34	230
Nylon 66	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ -\text{C} - (\text{CH}_2)_4 - \text{C} - \text{NH} - (\text{CH}_2)_6 - \text{NH} - \end{array}$	50	260
Poly(ethylene terephthalate)	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{C} - \text{C}_6\text{H}_4 - \text{C} - \text{O} - (\text{CH}_2)_2 - \text{O} \end{array}$	70	255
Poly(phenylene sulphide)	$-\text{S} - \text{C}_6\text{H}_4 -$	88	290
Poly(ether ether ketone)	$-\text{O} - \text{C}_6\text{H}_4 - \text{O} - \text{C}_6\text{H}_4 - \text{C}(=\text{O}) - \text{C}_6\text{H}_4 -$	145	334
Poly(tetra-fluoro-ethylene)	$\text{CF}_2 - \text{CF}_2$	125	345

Table 2. Amorphous engineering plastics

Material	Molecular formula	Glass transition temperature (°C)
Polycarbonate	$-\text{O} - \text{C}_6\text{H}_4 - \text{C}(\text{CH}_3)_2 - \text{C}_6\text{H}_4 - \text{O} - \text{C}(=\text{O}) -$	140
Polysulfone	$-\text{O} - \text{C}_6\text{H}_4 - \text{C}(\text{CH}_3)_2 - \text{C}_6\text{H}_4 - \text{O} - \text{C}_6\text{H}_4 - \text{S}(=\text{O})_2 - \text{C}_6\text{H}_4 -$	187
Polyarylate	$\text{O} - \text{C}_6\text{H}_4 - \text{C}(\text{CH}_3)_2 - \text{C}_6\text{H}_4 - \text{O} - \text{C}(=\text{O}) - \text{C}_6\text{H}_4 - \text{C}(=\text{O}) -$	192
Poly(phenylene ether)	$-\text{O} - \text{C}_6\text{H}_2(\text{CH}_3)_2 -$	210
Polyether sulfone	$-\text{O} - \text{C}_6\text{H}_4 - \text{S}(=\text{O})_2 - \text{C}_6\text{H}_4 -$	225
Polyetherimide	$-\text{O} - \text{C}_6\text{H}_4 - \text{C}(\text{CH}_3)_2 - \text{C}_6\text{H}_4 - \text{O} - \text{C}_6\text{H}_4 - \text{N} - \text{C}(=\text{O}) - \text{C}_6\text{H}_4 - \text{N} - \text{C}(=\text{O}) - \text{C}_6\text{H}_4 - \text{O} -$	200

Table 3. Representative properties of selected thermoplastic resin matrix materials

Property	Unit	Polymer/supplier							
		Polyimide Du Pont		Polyamide Du Pont	Polyamide imide Amoco Torlon C	PPS Phillips Ryton	PEEK ICI AFC-2	Nylon 66 Du Pont	PET Du Pont
		K	I-H						
Specific gravity		1.37	1.31	1.14	1.38	1.36	1.30	1.14	1.38
Glass transition temperature	°C	195	255	145	135	88	145	50	75
Melting temperature	°C	n.a.	n.a.		n.a.	290	334	260	255
Processing temperature	°C	371	371	315	350	325	390	290	290
Mechanical properties at ambient tensile strength	MPa	103	110	103	138	76	84	83	69
Tensile modulus	GPa	2.38	2.86	3.17	3.30	3.31	3.65	3.10	2.83
Tensile elongation	%	7	11	27	25	2.20	46	60	50
Fracture toughness	kJ/m ²	6.3	14		3.3				
Solvent resistance		+	+		+	+	+	+	
Price range	\$/lb	20	20	2	20	3	28	2	2

Source: Ullmann's encyclopedia of industrial chemistry, Vol. A-7, pp. 369-410.

Table 4. Property profile of the thermotropic LCPs

Property	A-130	C-130	A-515	A-420	A-652
<i>Technical</i>					
Tensile strength, MPa (D-638)	200	165	180	140	170
Tensile modulus, GPa (D-638)	17	16	12	20	10
Tensile elongation, % (D-638)	2.2	1.9	4.4	1.3	6.9
Textural modulus, MPa (D-790)	15	15	10	19	10
Notched izod impact strength, J/m (D-256)	135	120	370	100	130
Specific gravity (D-792)	1.57	15.7	1.48	1.88	1.54
<i>Thermal</i>					
T(1.82 MPa) C(D-648)	230	240	188	225	185
Coefficient of linear thermal expansion	Nil	Nil	Nil	Nil	Nil
<i>Chemical</i>					
Resistance to chemicals	Very good	Very good	Very good	Very good	Excellent
<i>Electrical</i>					
Electrical characteristics	Excellent	Excellent	Excellent	Excellent	Excellent
<i>Consistency/Processability</i>					
Consistency	Excellent	Excellent	Excellent	Excellent	Excellent
Processability in injection blow molding & extrusion	Easy	Easy	Easy	Easy	Easy

The most famous commercial example of LCP is the aromatic amide fibre, Kevlar, with mechanical performance better than steel. Kevlar fibres represent lyotropic LCPs meaning those polymers that exhibit liquid crystallinity in solutions. Thermotropic liquid crystal polymers, recently introduced by

Hoechst-Celanese and Dartco are melt processable. The typical properties of the Celanese LCPs are given in Table 4.

The existing lyotropic aramid and thermotropic polyester fibres exhibit tensile moduli in the range of 9-17 MPa depending on the chemical compositions and

process conditions, compared with values of 0.9 - 1.8 MPa for conventional nylon and polyester. The coefficient of thermal expansion of these polymers is significantly lower than that of conventional isotropic polymers, particularly in the machine direction. Therefore, the shrinkage of molded parts is negligible and the molding cycle is much faster for the low viscosity LCPs.

2.2 Thermosets

The most common matrix materials used in PMCs are thermosetting resins such as unsaturated polyesters, epoxies, phenolics and polyimides. The representative properties of selected thermosetting matrix materials are given in Table 5. The research and development activities in thermosetting resins are aimed at improving the toughness, high temperature performance, processibility and moisture resistance of these materials. The materials and structures used for aerospace and automotive applications must not only be strong and

light-weight, they must be adequately tolerant of impact under rough end-use conditions. The thermosetting resins such as epoxies and bismilemides are inherently brittle because of their highly cross-linked structure. Significant improvement in the ductility and damage tolerance of these resins can be achieved by the use of thermoplastic modifiers², as illustrated in Table 6. The effectiveness of the modifiers in toughening the matrix is governed by considerations of secondary chemical interaction between the modifier and the matrix resin at the interface, and the dispersed phase domain size in relation to the length scales of crazes and cracks. The polyimide modifiers are chemically more compatible with epoxies than the polysulfone modifiers. Therefore the addition of 20 per cent PEI modifier leads to a two-fold increase in toughness and a four-fold increase in fracture energy of the base epoxies. Although the addition of polysulfone modifiers improves toughness of epoxies, the improvement is not as significant as with PEI. It may be noted that the addition of such

Table 5. Representative properties of selected thermosetting resin matrix materials

Property	Unit	Polymer			
		Epoxy Narmco 5208	BMI Ciba-Geigy XII-922	Polyimide natural starch thermid 600	Rigid polyester generic
Specific gravity		1.265	1.35	1.37	1.10-1.46
Glass transition temperature	°C	238	310	350	70-140
Processing temperature	°C	177	250	370	20-150
Mechanical ambient properties at					
Tensile strength	MPa	50	94	83	40.90
Tensile modulus	GPa	39	39	39	20-44
Tensile elongation	%	1.4	3.0	2.0	2.0
Fracture toughness	kJ/m ²	0.08	0.21		
Solvent resistance		+	+		+
Price range	\$/lb	10			

Source: Ulmann's encyclopedia of industrial chemistry, Vol. 47.,p. 369-410.

Table 6. Toughening of epoxies with thermoplastic modifiers

Property	Unmodified	20 % Polysulfone	20 % Polyetherimide
Flexural properties			
Strength, MPa	119	112	91
Modulus, GPa	3.2	3.1	3.2
Elongation, %	4.2	3.9	3.0
Toughness, kNm ² xm ^{1/2}	577	756	1,222
Fracture energy, J/m ²	105	183	461
Glass transition temperature, °C	250	235	235

compatible modifiers improves the toughness with only marginal drop in the glass transition temperature of the matrix polymer.

Unsaturated polyester resins are the preferred matrix materials for a large number of PMC applications in transportation, chemical industry, marine and energy sectors, because of their cost effectiveness and ease of processing. The toughness of unsaturated polyester resins can be improved by the use of impact modifiers such as carboxyl or hydroxyl terminated rubbers, either blended or reacted with the resins. The major disadvantages of these impact modifiers are poor matrix-to-modifier adhesion and their poor compatibility with the matrix resins which leads to coalescence of the modifier particles during the initial stages of curing. This would prevent the development of required size distribution of the dispersion modifier domains. This conventional approach of toughening involving the dispersion of an elastomeric phase is based on the principle of hindered crack propagation. Although this approach leads to improved toughness, it results in a significant drop in the modulus of the matrix materials. A novel approach for the toughening of unsaturated polyester resins has been demonstrated by Nadkarni and Pandit³. It involves the use of reactive liquid polymers (RLP) which are chemically incorporated in the polyester network during the curing process as illustrated in Fig. 1. The RLPs used are unsaturated polyesters based on polyether polyols and maleic anhydride. The use of the RLPs results in a homogeneous system wherein the energy dissipation required for improved impact resistance is effected through the segmental motion of the pendant chains. The aim is to toughen the polyester matrix resin without a significant loss of its modulus with the use of RLP, which is demonstrated in Fig. 2. The improvement in the notched izod impact, toughness, and fracture energy of the base unsaturated polyester matrix by the addition

of 10 per cent RLP based on PEG 200 is shown in Table 7. It may be noted that there is only a marginal drop in the glass transition temperature of the matrix and that the shear modulus in the glassy state is unaffected by the incorporation of the toughening modifier. It was observed that the toughening efficiency showed a minimum at a PEG pendant chain length of 25 Å.

The commercially available grades of polyimides and polybenzoxazoles can be used at temperatures upto 370 °C. However, further improvement in the high temperature mechanical performance of thermosetting matrix materials has been demonstrated by the use of fluorinated polyimides⁴. The fluorination significantly improves the thermal oxidative stability of the materials for continuous use at high temperatures.

In summary, the emerging trends in materials innovation mainly concern improving the toughness and high temperature performance of thermoplastic and thermosetting matrix materials used in PMCs.

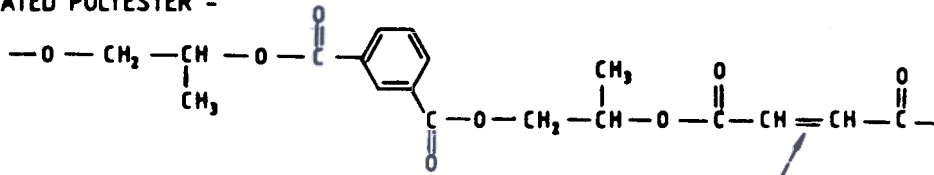
3. STRUCTURE DEVELOPMENT IN PROCESSING THERMOPLASTIC COMPOSITES

The consumption of composites in engineering applications has increased inspite of the oil crisis. There are two primary reasons for this. Firstly, the manufacturing processes for conventional materials such as glass, metals and paper, as also the conversion processes for fabricating products from these materials, are highly energy intensive because of the high working temperatures involved. The disadvantage of high feedstock costs that plastics face is therefore offset by the higher energy costs of conventional materials. Secondly, materials costs are normally of the order of 35 to 50 per cent of the overall cost of the plastic finished product. The influence of rising feedstock costs is thus diluted. Further, in a number of large volume applications, such as engineering parts, the cost

Table 7. Toughening of unsaturated polyesters with reactive liquid polymers

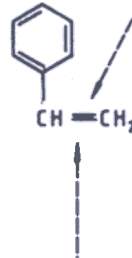
Property	Unmodified polyester	10% Reactive modifier
Shear modulus, dynes/cm ²	1.04 × 10 ¹⁰	.07 × 10 ¹⁰
Notched izod impact strength, kJ/m ²	0.72	1.10
Toughness, kNm ² xm ^{1/2}	641	2975
Fracture energy, kJ/m ²	270	1400
Glass transition temperature, °C	103	99

UNSATURATED POLYESTER -



CROSS-LINKING MONOMER -

STYRENE -



REACTIVE ADDUCT -

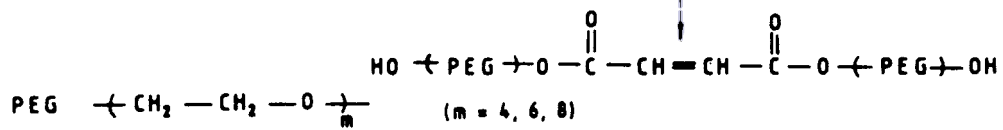


Figure 1. Toughening of unsaturated polyesters with reactive impact modifiers.

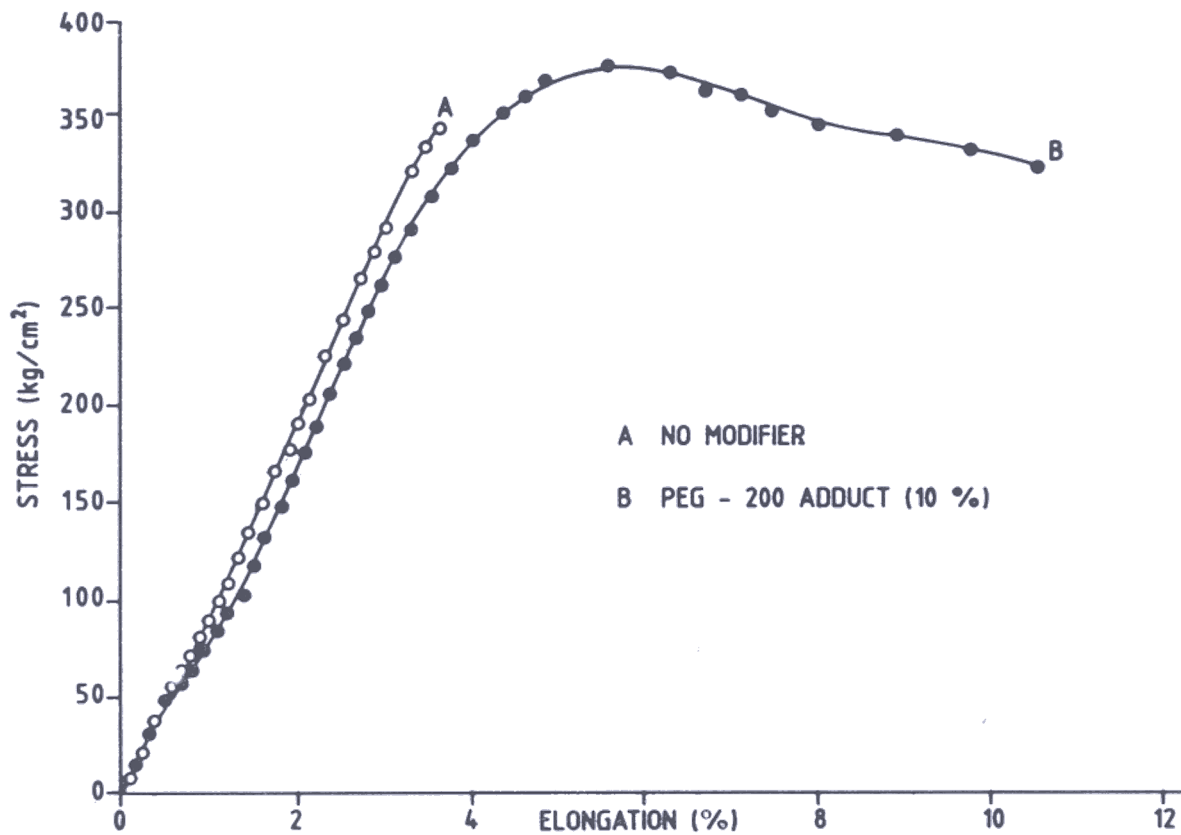


Figure 2. Tensile behaviour of toughened unsaturated polyesters resin.

effectiveness of a material is governed not merely by the material cost but also by the processibility and design flexibility offered. Plastics can compete favourably with low-cost high volume metal working processes because of the inherent economics of injection molding. Additional savings are often made because single-piece, multi-functional complex parts can be designed with plastics and produced in a single molding step, eliminating several metal components.

Injection molding involves melting of the polymer pellets in an extruder followed by injection of the thermally and mechanically homogeneous melt into a mold cavity under high pressure (approx 1000 atm). In the mold, the polymer solidifies and the part is demolded after a fixed time cycle. The entire molding cycle is completed in a short time period of the order of 1-2 min. During these operations, the polymer molecules, initially in a random coil conformation in the molten state, are subjected to a number of competing physical processes including shear flow induced molecular orientation during mold-filling, relaxation in the molten phase, cooling and solidification with or without concurrent crystallization. Similar processes occur in the other processing techniques such as film extrusion, fibre spinning, blow molding, etc., except the type of flow fields and cooling rates encountered by the polymer molecules would be different.

The structure development in polymer processing concerns the effect of the thermal and mechanical environment on the intermolecular and intramolecular changes in the polymer chain conformations. The manner in which the macromolecules are packed and oriented with respect to each other at the end of processing would determine the properties of the shaped articles. The interdependence of the properties, structure and processing parameters in polymeric materials is schematically illustrated in the form of a block diagram in Fig. 3. Thus, the challenge to the materials engineer, in the words of Tadmor and Gogos⁵, is "to design the processing steps in such a way that the desired conformations (or spatial arrangements at molecular scale) are achieved at high temperatures in the molten state and subsequently locked in as the processed article is cooled to use temperature".

Unlike metals, semicrystalline polymers exhibit a two-phase structure in the solid state, consisting of distinct crystalline and amorphous domains. The

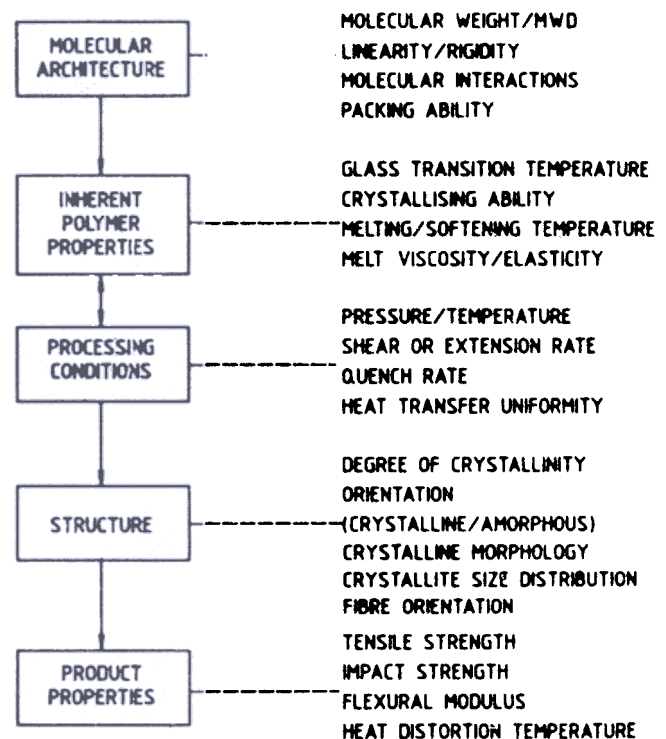


Figure 3. Processing-structure-property relations in polyesters.

volume fraction of the material constituting the crystalline phase is termed the degree of crystallinity. The basic structural unit in the crystalline domains is the folded chain lamella. The lamellar structure is formed by chain folding of a number of polymer chains. Any single polymer chain can enter and leave the lamella. Thus, a fraction of the segments of any chain forms the crystalline phase, whereas the remaining segments constitute the amorphous phase. This feature gives rise to the interconnections between the two phases essential for stress transfer during deformation. The lamellae, in turn, pack into a spherical geometry giving rise to spherulites which represent a super-molecular structural unit in polymers crystallized from melts (Fig. 4). The nature and extent of the interconnections of tie molecules determine the stress-strain behaviour of the processed article.

The stress fields and orientation effects experienced by the polymer molecules in the molten state influence both the crystallization kinetics and the nature of the supermolecular morphology exhibited in the form of either spherulites, row nucleated axialites, or shish-kebab structures.

Thus the parameters defining the structure in the solid state of a semi-crystalline polymer include the degree of crystallinity, lamellar or crystallite thickness,

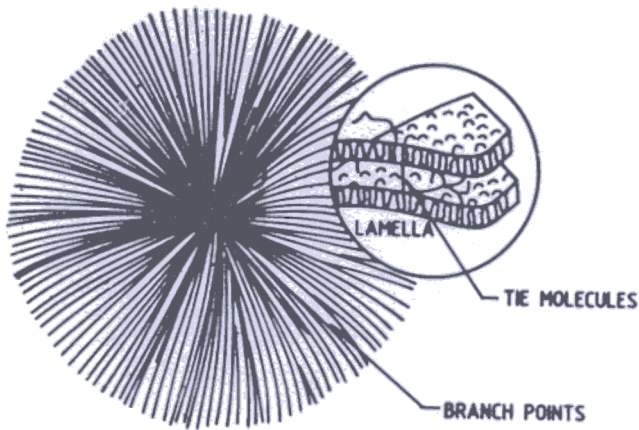


Figure 4. Schematic representation of spherulitic structure.

type and size of the supermolecular morphology (for example, spherulite size distribution), and the nature and extent of tie molecules.

In the case of semi-crystalline engineering plastics such as nylons, thermoplastic polyesters, polyphenylene sulfide (PPS) and polyether-ether-ketone (PEEK), crystallization of the polymer takes place during the molding cycle. The rate of cooling in the mold has considerable influence on the degree of crystallinity and the resulting morphology, which in turn affects the mechanical properties and dimensional stability of the molded part. Therefore, it is necessary to optimize the injection molding parameters such as the melt temperature, mold temperature and demolding time for a given product in the context of the relation between the competing rate processes of crystallization and cooling.

The primary consideration in specifying the molding conditions is that the crystallization of the polymer should be complete throughout the cross-section of the molded part before demolding. In the case of complete and non-uniform crystalline morphology, shrinkage and warpage of the molded part would result, participating when the molded part is exposed to temperatures above the glass transition temperature of the polymer. It is therefore critical to manipulate the cooling conditions in such a way that the polymer spends adequate time in the mold at temperature over which the rate of crystallization of the polymer is fast, so that complete crystallization is ensured before demolding. Thus the inherent crystallization kinetics of the polymer is the limiting factor in specifying the mold cycle time, although a short mold cycle is preferred to increase productivity.

The rate of polymer crystallization is strongly dependent on the temperature of crystallization, exhibiting a maximum over a narrow range of temperatures intermediate between the melting point and the glass transition temperature. The isothermal crystallization kinetic data for the 40 per cent glass fibre reinforced grade of PPS, an engineering plastic, are shown⁶ in Fig. 5. The minimum crystallization time over the temperature range of 140 to 205 °C is of the order of 10-15 s. Therefore, in order to obtain a molded product with fully developed crystallinity, the molding conditions are to be so defined that the polymer spends about 15 s over this temperature range.

The main process parameter used for manipulating the cooling temperature profile is the mold temperature. The melt temperature and the injection pressure are generally specified on the basis of rheological

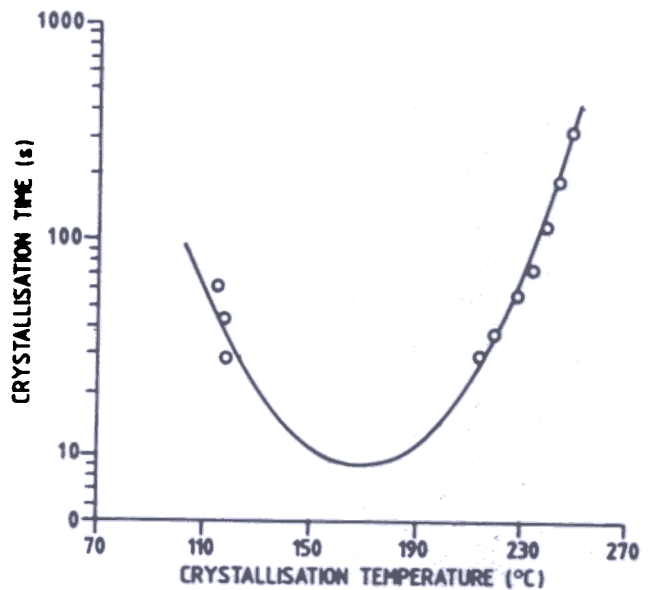


Figure 5. Isothermal crystallization kinetic data for glass fibre reinforced poly(phenylene sulfide).

considerations pertinent to mold filling. Optimization of the mold temperature and mold cycle time is normally carried out by molding trials and subsequent testing of the molded specimens produced under different processing conditions. This trial and error approach is costly and time consuming. It can be circumvented by using a methodology based on the understanding of the structure development in molding semicrystalline polymers and involving the superposition of the polymer crystallization kinetics and the computed cooling temperature profiles⁷.

Table 8. Effect of mold temperature on conditions of crystallization and properties of PPS⁷

Property	Set A	Set B
Mold temperature, °C	135	38
Range of quench rates, °C/min	60 to 660	1020 to 1620
Crystallization temperature T_c , °C	158-200	125-150
Required crystallization time, s	9.5-13	11-33
'Dwell time' over T_c , s	9	1.5
Degree of crystallinity, %	50	5
Unnotched izod impact strength, J/m	175	312
Notched izod impact strength, J/m	58	74
Heat distortion temperature at 1.8 MPa, °C	243	230

The data in Table 8 indicate that the molding conditions in Set A, wherein the mold temperature was held at 135 °C, are conducive to developing equilibrium crystallinity in the molded part. For Set A, the crystallization temperatures (158 - 200 °C) lie within the range of fast crystallization for PPS (142 - 205 °C) and once crystallization is induced, the dwell time spent by the polymer over the relevant temperature range t_d , is comparable to the crystallization time, t_c . On the other hand, for Set B, the range of crystallization temperatures is narrow and the dwell time of the polymer over this range is significantly shorter than the corresponding crystallization time. Thus little crystallinity development would take place under the molding conditions of Set B, wherein the mold temperature was held at 38 °C. The conclusions are consistent with experimental results of Brady⁹ who has reported a crystallinity index of 50 per cent for PPS molded at a mold temperature of 135 °C and a crystallinity index of 5 per cent for molding at mold temperature of 38 °C. This lack of crystallinity in Set B is responsible for the lower heat distortion temperature and higher impact strengths.

It can thus be concluded that the above method involving the superposition of the basic crystallization kinetic data and the computed cooling temperature profiles can be used effectively to arrive at molding guidelines without extensive molding trials. The molding parameters such as the mold temperature may be specified *a priori* by such an analysis, in order to obtain a desired morphology from property considerations; the molding conditions so specified may then be 'confirmed' by actual molding trials. The proposed method would therefore allow simulation of injection molding of any polymer on the basis of its

thermal properties an crystallization data, and the mold geometry details.

4. INTERFACE AND INTERPHASES IN PMCs

The mechanical properties of PMCs are directly influenced by the efficiency of stress transfer across the fibre-matrix interface. The development of proper coupling agents and process technology for application of these surface treatment chemicals on to the fibre surface represent active areas of research in the development of PMCs. A variety of silane and titanate coupling agents are commercially available for improving the adhesion and interfacial stress transfer between the matrix and reinforcing fibres. The type of coupling agents has to be carefully selected based on considerations of secondary chemical interaction between the fibres and the matrix materials. Recently Wang and co-workers have demonstrated the novel concept of catalytic grafting for improving the interfacial adhesion¹⁰. The technique involves chemical anchoring of catalyst on to the surface of the reinforcing fibres which would initiate polymerization of the matrix materials on the fibre surface.

In the processing of semi-crystalline thermoplastic composites, a distinct two-dimensional micro-structure has been observed near the fibre surface because of the heterogeneous surface nucleation. The very high nucleation density on the fibre surface leads to a columnar growth of the lamellae because of the restricted growth in lateral directions. The presence of such a trans-crystalline interphase influences the stress transfer from the matrix to the reinforcing fibres. The mechanism by which trans-crystallization occurs is not fully understood. The presence of trans-crystallinity has been reported to be affected by the fibre material, the

the second category. The third category of high performance PMCs would include speciality matrix materials such as polyimides, PEEK, etc with carbon, graphite, aramid and ceramic fibres. It should be recognised that the focus of development efforts in materials, processing and applications research has to be different for the three categories of PMCs.

In India, although the first category of PMCs based on GRPs are commercially established, considerable development efforts are needed to upgrade the material and product consistency, processing efficiencies and meaningful applications research. Although some R&D projects are in progress in the high performance PMCs, mainly in the Defense and aerospace sectors, these are limited to thermosetting matrix materials. There is need to initiate efforts for developing both technical and production engineering capabilities in the use of PMCs based on FRTPs.

In order to quickly bridge the technological gap between the developed world and our country, a backward integration approach may be followed. Thus, emphasis should be given, in the initial stage, to the processing and product/applications development of engineering components produced from imported materials. This step would lead to the development of a market for the high performance materials in the country and could then serve as a catalyst for future commercial manufacture of these materials in India at capacities that would allow economy of the scale.

6. INDIGENOUS DEVELOPMENT APPROACH

Although a variety of composite materials are available in the world market, in view of the limited availability of these materials in India and their high cost, there is a need for evolving a systematic materials engineering approach to assess and demonstrate the potential of composites in engineering applications in the country. The approach should involve identification of specific applications in the various sectors such as transportation, construction, water management, effluent treatment, etc followed by product design exercise. On the basis of the performance requirements in the applications and the cost targets, composite materials may be selected or developed to meet the targets. After the materials selection or development, the next step is to develop the processing technology for converting the material into the product.

However, it has not been indigenous non-availability of materials so much as the absence of an applications research programme, that has held up the diffusion of PMCs in engineering applications in India. In the US, Europe, and Japan, the large companies manufacturing engineering plastics have, under a single roof, both the facilities and the interdisciplinary expertise required for polymer synthesis, characterisation, processing science and technology development, product design and applications research. This model is not workable in the Indian context. Realising this, National Chemical Laboratory (NCL), Pune has successfully demonstrated and instituted an interactive project approach with the involvement of end-user of the engineering component, molder and material manufacturer, thus completing the innovation chain. By following thus approach, composite components for the scooter engine have been successfully developed and commercialised in collaboration with Bajaj Auto Ltd, the end-user; Kirloskar Kisan Equipment Ltd, the molder; and BM Thakkar & Co Ltd, the manufacturer of the thermoplastic composite material developed by NCL.

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