

Chapter 2

Design for Multicomponent Materials

**Jaideep Adhikari, Sukanya Chowdhury, Prosenjit Saha
and Jin Kuk Kim**

2.1 Introduction

Designing is the primary phase of the life cycle of a product or material. Therefore, rationalization between process design and subsequent mechanisms along with the performance of the material has been tried out by several researchers for many years [1]. Defining the architecture of the multi components is the first step towards designing which includes refinement and optimization of the process in brief [2]. Material selection is also one of the most important stages of product design keeping in view about its end applications. Improvement in property of materials inevitably increases its cost. So, designers nowadays tend to correlate between cost and technical specifications of a material by optimizing several key parameters. To make a product commercially viable thus integration between cost and property as a single function is required [3].

Designing is a function of constraints as certain dimensions remain fixed according to the end uses. Performance of material is evaluated according to their mechanical, electrical, thermal, chemical, and optical properties. Mapping between these properties through different ranges reveals that a single material is not suffi-

J. Adhikari · P. Saha (✉)
Indian Institute of Engineering Science and Technology—Shibpur,
Dr. M.N. Dastur School of Materials Science and Engineering,
Howrah 711 103, WB, India
e-mail: senjitiitkgp@gmail.com; prosenjit@matssc.iiests.ac.in

S. Chowdhury
Environmental Science Department, Asutosh College,
University of Calcutta, Kolkata 700026, India

P. Saha · J.K. Kim (✉)
Department of Materials Engineering and Convergence Technology,
Gyeongsang National University, Gyeongnam, Jinju 660-701, South Korea
e-mail: rubber@gnu.ac.kr

cient for fulfillment of every aspects of its application. Thus, multicomponent materials come into the scenario which copes up a system inadequacy about a specific property by incorporation of different material into the system which is superior in that particular property [4]. So combining several different properties into a single material is the main characteristics of multicomponent material. The subject is of great relevance as real life structures or problems involve multiple components and thus they are interrelated since change in one component has its effect on the others also. Thus a general methodology is required which can tackle several shortcomings considering the multi component system as a whole [5].

2.1.1 Fundamentals of Materials Processing and Design

The shift from conventional materials towards high end polymeric multicomponent materials is based on the availability of subsequent economic advantages. The primary parameters that ensure the substantial changes in technological trend for designing multicomponent materials mainly include processing and fabrication, corrosion resistance, low specific weight, diverse options of colours, low thermal and electrical conductivity, high dielectric strength and good toughness with degradation resistance to alkali, acid and moisture etc. [6] Multicomponent polymeric material processing basically deals with advanced polymer blends, composites, nano composites and interpenetrating polymer networks. A large variety of these multicomponent comes by combining different polymers or by adding different types of fillers ranging from nanometer, micrometer to larger particulates. The filler may be fiber or combination of both particulate and fiber as reinforcement leading to something like multi component system. Fillers improve tensile and compressive strength, abrasion resistance, dimensional stability etc. of the materials. Apart from filler some foreign substances or additives viz. plasticizers, colorants, stabilizers, fire retardant, antistatic agents, cross linking agents; blowing agents (for cellular or expanded products) are also intentionally introduced to the system for having a modified property. Different potential processing techniques like compression molding, injection molding, thermoforming, pultrusion etc. are successfully employed to shape the polymers. Modification of these processes is successfully carried out by first modelling them appropriately. Commercial software packages with advanced modelling successfully demonstrate different macroscopic parameters viz. stress, flow rate, viscosity etc. But often correlation between morphological properties with multicomponent has been neglected in the design stages [7].

Traditional approach for extending material property space suggests modification of new polymer chemistry with new composition. Imparting such new modification approach is quite costlier, time consuming, and uncertain, therefore using multi-component material with superposition of properties of different material has been tactfully used for targeted properties [4]. For starting a design problem a designer starts with basic steps which are illustrated in Fig. 2.1. Design requirements involve mainly four stages [8]

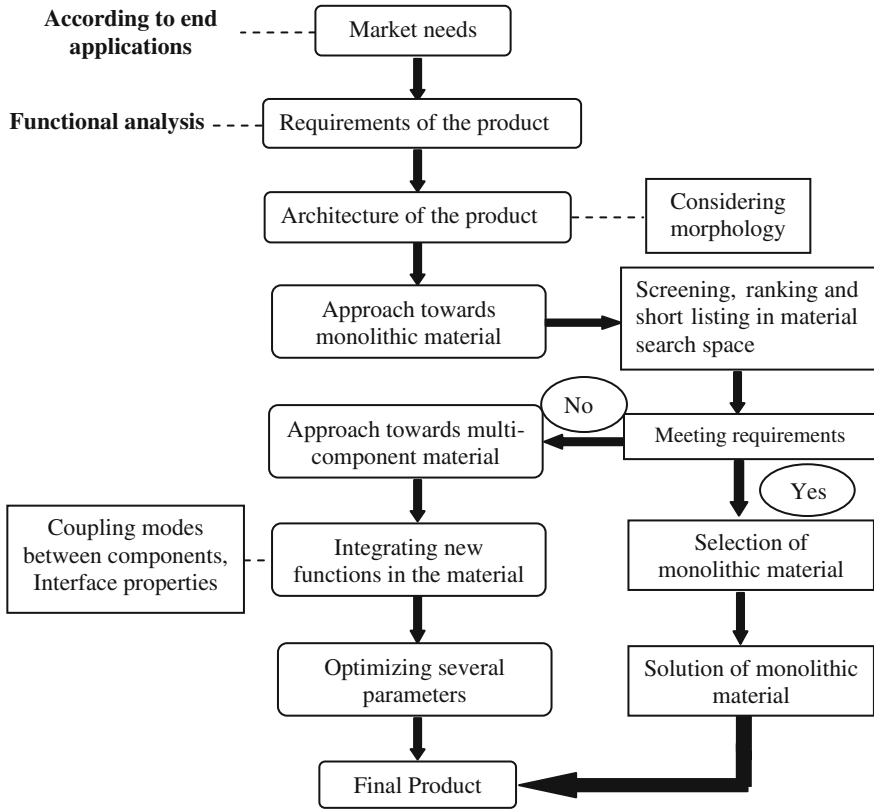


Fig. 2.1 Basic steps for designing

- Establishment of correlation between design requirements and specification of materials.
- Elimination of unsuitable candidates (materials).
- Gradation of greatest potential material.
- Selecting ideal material considering strengths, weaknesses, and history of use and future potentials.

Designer needs to evaluate and select the monolithic materials as an answer of a set of material requirements, however upon failure of such strategy a multi material must be designed by integrating new functions available to multicomponent materials. Thus, optimizing the several parameters of a multi material must fulfil the requirements of end-users.

Necessity of multicomponent materials:

Multicomponent materials are combination of materials that cannot be disassembled and the materials must be in a reasonable fraction of volume and smaller in

dimension in comparison to the system in which these are engaged [1]. The basic reason to go for a multicomponent material has already been discussed earlier.

Selection strategy of materials plays a vital role in designing the process. An optimization tool performs by analyzing a set of given inputs with their constraint equation followed by converting them to a set of outputs. Some previously known outputs of the materials and processes are used to perform as a transform functions and fit them to a best possible desired design requirements. A designer considers some macro objectives for a competitive product such as (a) minimizing mass; (b) minimizing volume (sometimes); (c) minimizing manufacturing costs and increasing productivity; (d) minimizing environmental impact etc. On the basis of these guidelines designer theoretically performs three tasks:

- Incorporating user needs into material features (technical and non-technical requirements).
- Formulation of performance matrices on basis of material key features inventory.
- A search procedure-structured material selection method
 - (a) Explore a solution space,
 - (b) Identify materials that meet the constraints,
 - (c) Rank them by their ability to meet the requirements.

An introduction of term strategy opens up the scope for material selection. Thus material selection is not just only confined to a method but a well-defined plan and action on a long term basis keeping in mind on the success of the product in the market. Consequently it also effects on the success of production houses against competitive forces in terms of market evaluation. Strategy is like a transfer function that converts a set of inputs into a set of outputs. Selection strategy in respect of material selection is briefly discussed in Fig. 2.2.

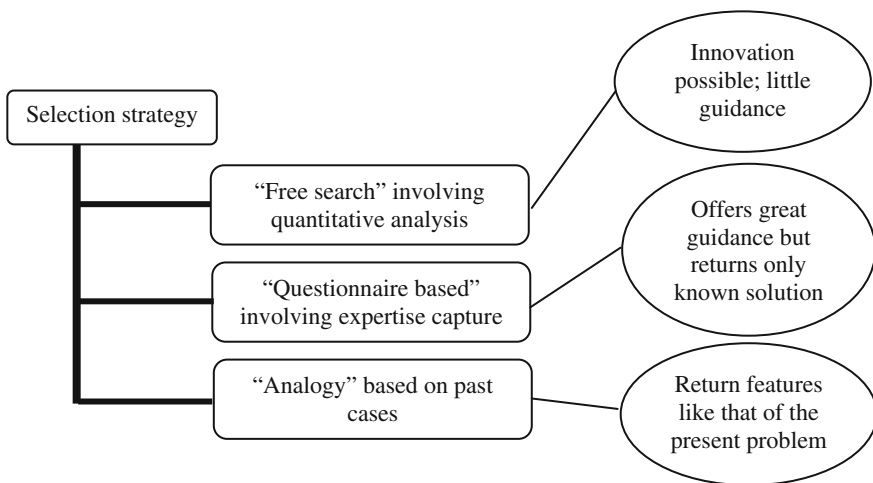


Fig. 2.2 Selection strategy [8]

Quantitative analysis is fast, efficient, flexible etc. but requires very precise degree of input. Questionnaires are more or less structured set of decisions usually works like a set of family tree. But questions should be properly targeted in each step; otherwise it will lead to a vague conclusion. Previously solved problems are used as library of transfer function of third case but difficulty rise in correlating these solutions with the present design problem.

After strategy it is necessary to consider some selection rules for choosing an appropriate multi component system, in view of its end application. Selection of a multi component material and process can be explained through an inverted pyramid process as shown in Fig. 2.3.

Final selection of material and process is performed on the basis of ranking and screening out of unpotential candidate. Researchers proposed different screening methods for selection of materials. The screening methods are mainly-

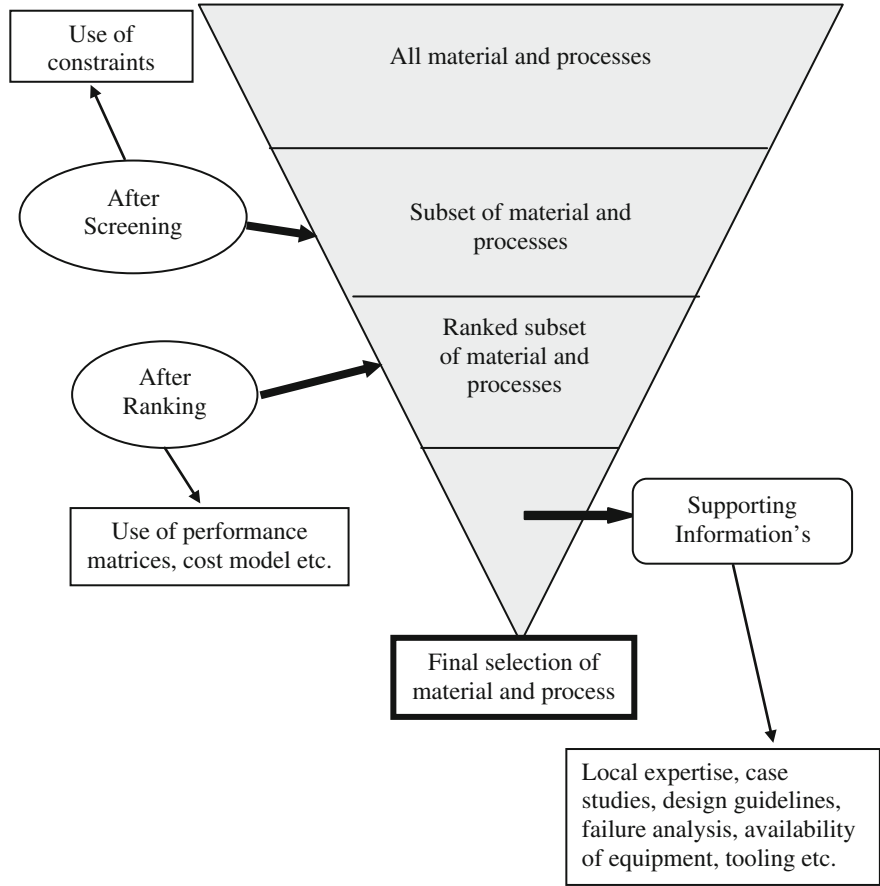


Fig. 2.3 Steps for selecting a material and process [9]

- Cost per unit property method (considers most critical property ignoring others).
- Chart method (useful for initial screening with respect to mechanical performance).
- Questionnaire method (ranking cannot be possible but useful for achieving optimal design solution).
- Materials in production selection tools (low translation percentage between user interaction and material property).
- Artificial intelligence method (appropriate tools for searching) [10].

Performance matrices are used for ranking of materials. Considering environmental effects nowadays it is essential to develop a sustainable and recyclable product. Reduction of waste stream, lesser use of earth resources are also considered as constraints for material selection rules. So, for development of a sustainable product apart from economic aspects social and environmental aspects also come under the selection guidelines [11]. An economical aspect mainly includes purchase, process, transport, disposal cost (Fig. 2.4).

Selection of material is a step forward towards achieving the goal. The very next stage is optimization. Optimization of several parameters is done by incorporating several tools to achieve a well-processed product life cycle. It is important to conceptualize and embody these processes in a single design. More than often incorporation of different system in a single material improves its properties in a particular way but deteriorate in another way. Thus the need of optimizing several parameters is felt and the short comings of multi-component material are searched. The process is briefly discussed through a flow chart in Fig. 2.5. Search for solution of multi component materials is performed in view of components, architecture, adapted interfaces and pre-established solutions.

Different configuration of multi component material is carried out under several optimization tool packages some of them are tools for dividing up material requirements, topological and screening tools, architecture selection and optimization tools etc. Multi criteria decision making (MCDM), Technique of Ranking Preferences by Similarity to Ideal Solution (TOPSIS) method are widely used in

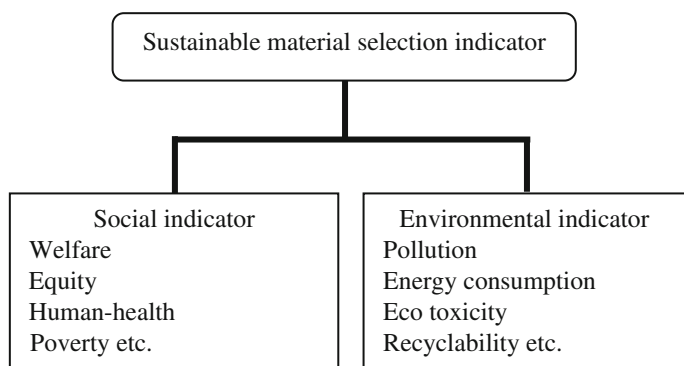


Fig. 2.4 Sustainable material selection indicator [11]

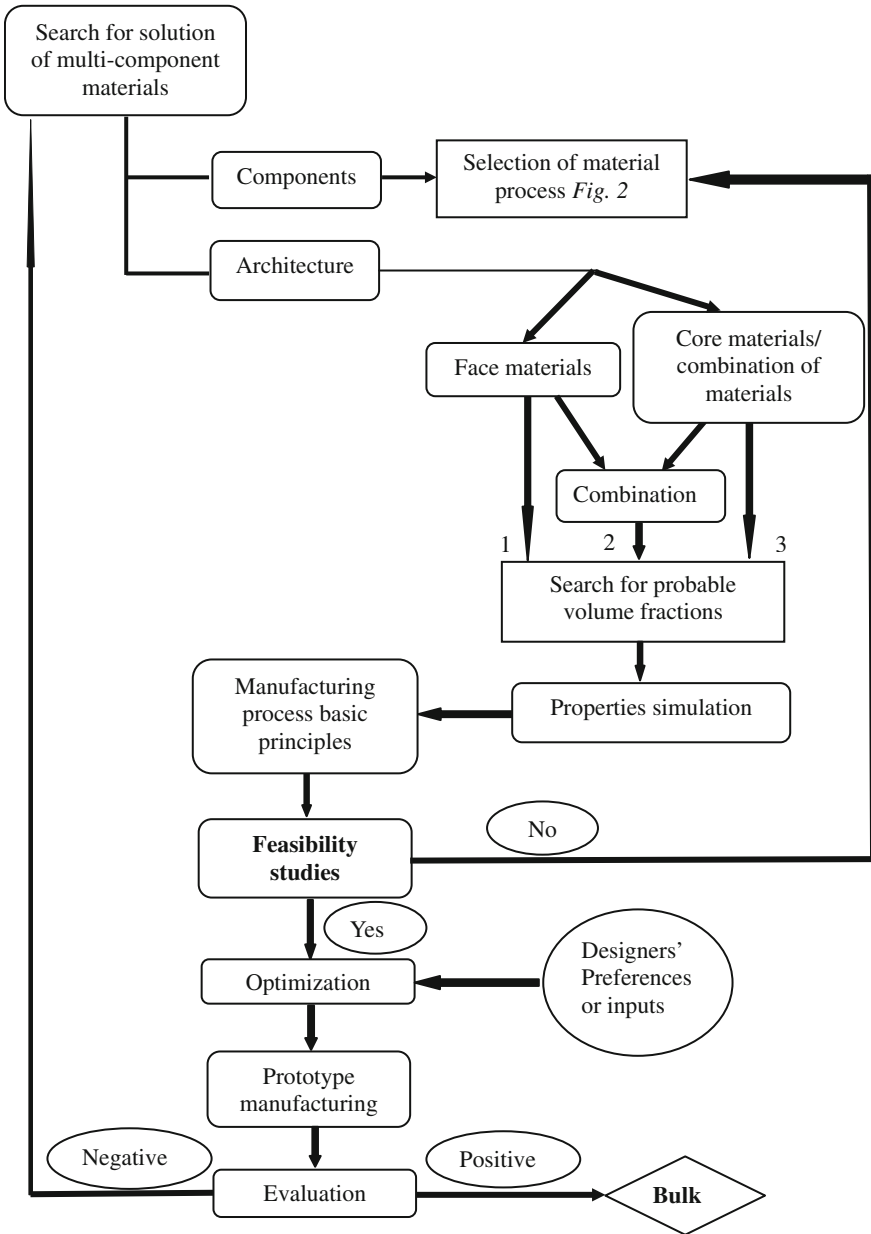


Fig. 2.5 Solution of multi component material

serving superior material requirements. Engineering problem with high degree of complexities has been sorted out nowadays with hybrid methods such as TOPSIS along with Analytical Hierarchy Process (AHP) or sometimes in combination of

Genetic Algorithm (GA) with Artificial Neural Network (ANN) for optimization of a process. ELimination Et Choix Traduisant la REalité (ELimination and Choice Expressing REALity) or ELECTRE method is also a multi criteria decision analysis tool often used for material selection of bipolar plates for polymer electrolyte membrane fuel cell (PEMFC) [12, 13]. One recent approach in process control for optimizing polymer composites properties is performed by fuzzy logic controller system. Reduction of temperature variation is obtained by fuzzy logic controller [14] across melt flow of polymer extrusion. A synopsis of process monitoring by Raman spectroscopy, and adaptive Neurofuzzy approach helps to successfully monitor molecular changes in real time. This soft computing technique has been successfully applied to solve the problems of polymers materials during manufacture of thermoset based composites typically for epoxy resins [15]. Researchers have also tried fuzzy logic for prediction of total specific pore volumes of derived polymers [16]. ANN based soft sensor are utilized by a group of researchers [17] for control on viscosity of real time industrial polymerization process of polyethylene terephthalate (PET). Some commercial software packages like ABAQUS (a finite elemental analysis suite), MOLDFLOW (used for injection moulding) are often used for assistantship in micro injection moulding. Optimization of moulding tools is performed with this kind of commercial tools [18]. Temperature distribution can be simulated by ABAQUS package tool in micro injection moulding system. Above all success of a process also depends on the clarity of design, any shortcomings or design errors in selection rules or any other steps during processing of materials leads towards a totally different and undesired product.

2.1.1.1 Influence of Rheology on Design

Rheology is the science of deformation and flows under external stress. It is critically performed for understanding and interpreting mechanical behavioural pattern under a given temperature. The deformation generally caused by the external forces is of three types-tensile force, compressive force and shear force. Under processing and during performance a polymeric multi-component experiences these forces. Flow behaviour of polymeric materials is also governed by the rheological properties while processing under the molten state. Rheology is an important parameter for designing as it correlates with the structure of a multi-component. Rheological properties of a material are sensitive to structure in certain aspects and are easier to use than the conventional analytic method viz. nuclear magnetic resonance [19]. Rheological properties are dependent on several conditions mainly (a) strain rate, (b) polymeric creep (under a static load, the deformation of polymeric material increases with time, (c) Stress relaxation (During a constant deformation process the stress required to maintain the deformation decreases with time, (d) mechanical strain energy of a system can which is convertible to heat energy is accessed by the measure of internal friction. Any polymer system typically shows an in-phase as well as an out-of-phase components when subjected to sinusoidal stress. The phase lag (angle) between the stress and strain is a measure of the internal friction. At normal

temperature creep, stress relaxation phenomena are insignificant to metals so they are usually neglected during design consideration at room temperature. They are taken into account when they are close to their recrystallization temperature (usually $0.4\text{--}0.6 T_m$). But for multi component polymeric material particularly for structural applications they should be taken into account at the design stages [20].

For a heterogeneous system like multi component polymeric material structure and property can be correlated with rheological measurements. According to force exerted during tests rheological properties can be divided into two types: Static rheological measurements performed under steady shear flow motion i.e. under certain stress or strain and Dynamic rheological measurement performed under oscillatory shear flow i.e. under periodic stress or strain. During static rheological testing a multi component polymeric materials continuous effect of stress is hardly obtained as this testing leads to change even breakage of macromolecular segment. Birefringence, dichroism are optical properties of a material usually performed to predict the orientation of the aggregates. So static rheology is integrated with optics to detect shear stability and orientation of the aggregates and segments in a flow field as flow birefringence and flow dichroism [21].

Dynamic rheological testing can be effectively carried out for the measure structure/morphology of multi-component as these testing are done under small strain amplitude. Dynamic rheology testing is believed to be a preferential method because of materials exposed to the testing processes is not destroyed under small-strain amplitude. But care has to be taken such that the working condition remains under linear viscoelastic region.

For determining the linear viscoelastic region (LVR) amplitude sweep is performed over a stress or strain range. Stability can also be predicted from a plot of complex shear modulus versus shear stress under amplitude sweep. After prediction of LVR frequency sweep is performed to determine the nature of material. Storage modulus G' is evaluated from amplitude sweep and loss modulus G'' from frequency sweep. The complex modulus that is overall material resistance to deformation $G^* = G' + iG''$. The ratio of loss modulus to storage modulus is predicted as tan delta parameter which is equal to G''/G' and gives a measure of the viscous portion to the elastic portion of a polymeric melt. If

$\tan(\delta) > 1$ ($G'' > G'$) (liquid or 'sol')

$\tan(\delta) = 1$ ($G' = G''$) (viscoelastic or 'gel point')

$\tan(\delta) < 1$ ($G'' < G'$) (solid or 'gel')

$\tan(\delta)$ is especially helpful in measuring sol-gel transition point. Viscosity, strain rate, Deborah number is some very common rheological parameters and should be considered while designing multi-component.

Smart fluids such as magneto rheological suspension consist of micrometer-sized particles (which can be magnetized), dispersed in suitable carrier liquids. In the absence of an external magnetic field this material behaves like Newtonian fluid but apparent suspension viscosities can be increased by several orders of magnitude under external magnetic field. Magneto-moments aligned in the direction of

external field and causes strong magnetic interactions which in turn causes aggregation of complex networks. Thus these structures can withstand a certain amount of shear stress and can be characterized by a high yield stress values. Magneto rheological fluids find their usage in automotive clutches, brakes for exercise equipment, polishing fluids, seat dampers, prosthetic knee damper, actuator systems, shock absorbers etc. [22, 23]. Thermo-oxidation temperature region of polymeric material (generally for polyolefin) can be predicted by dynamic rheological behaviour of multi component systems such as high density polyethylene (HDPE)/carbon black (CB) composite system [24].

- Electrically conductive polymer matrix composites have attracted researchers for its unique electrical and mechanical properties. Filler concentration and the state of the filler dispersion are the two most important influencing parameters for these composites. For conductive composites a continuous conductive chain is required which is dependent on some critical concentration of fillers. This phenomenon is taken care in terms of percolation theory. Dynamic rheological measurements believed to be a good method for dealing with filler dispersion. Homo-polymers in low-frequency regions exhibit the dynamic storage modulus (G') and dynamic loss modulus (G'') are proportional to the frequency squared (ω^2) and to ω . $G' \propto \omega^2$ and $G'' \propto \omega$. For filled polymer melts dynamic viscoelastic functions exhibit a special response. Thus estimation of the agglomeration for conductive polymer composites through dynamic rheological measurements is carried out by correlating electrical percolation with viscoelastic percolation [25].
- Viscosity, surface tension and conductivity are three main solution parameters of nano fiber preparation by electro spinning technique. Generally higher viscosity smoothers formation of fibers. Rheological study of polymer solutions in the bulk and at the interface finds correlations between those properties. For chitosan or alginate filled with poly(ethylene oxide) (PEO) polyblend it is found that interfacial rheological parameters have much more influence than the bulk. Conductive system in the bulk displaying predominant plasticity over elasticity is found to be suitable for electro spinnability [26].
- Composites manufactured from compression moulding technique undergo an anisotropic viscous behaviour of matrix material. Non-Newtonian flow behaviour is often modelled for successful distribution of polymeric melt in the mould while fabricating composites like sheet moulding composites (SMC) [27]. Compression moulded polymer matrix are often porous. Mould composite friction effects are usually neglected in rheological studies thus new modelling technique proposed by the researchers taking compressibility and mould-composite friction into account. Outer layers with higher polymer density of fiber reinforced composites act as lubricating layers that are squeezed and sheared near the mould surfaces. However, the core of the composite filled with fiber deforms like extensional plug flow [28].

- In shear induced crystallization of polymers the effect of viscosity is negligible but with increasing crystallization, viscosity also increases. So crystallization time is modelled with rheological properties. It is performed mainly for polyolefins [29].
- Phase separation of poly blends, different chain segments of block co-polymer (micro-phases) have also relationship with their rheological behaviours.
- Rheological measurements while liquid to solid transformation takes place are an important parameter as it involves gelation. The prediction of gel point gives access to working time (which can be modified by delaying gelation) for fabrication of multi-component.

Rheological measurements are made in conjunction with the product quality and efficiency (ex. normally if thermosetting resin is stored for a longer period of time its viscosity increases). Viscosity is the principal parameters for rheological measurements. A designer can predict product dimension from viscosity such as liquid, semi-solid. Designers can predict pumpability and pourability of polymeric material, performance in a dipping or coating operation, or the ease with which it may be handled, processed, or used. Detecting changes in colour, density, stability, solids content, and molecular weight can also be interpreted by rheological measurements. Thus rheological experiments are useful for (a) characterization, (b) determination of processability, (c) failure analysis (sometimes for extrusion, injection moulded samples), (d) simulation (gives data as input for modelling and simulation).

2.1.1.2 Influence of Shear Rate on Design

A liquid is a material in which strain is a function of both stress and time. Shear rate is defined as the ratio of shear stress to strain rate. Thus shear rate or specifically shear strain rate is an influential parameter in engineering design. For a Newtonian fluid shear rate versus shear stress plot shows a straight line passing through the origin. Dilute suspension of particles in this type of fluid also tend to behave like Newtonian fluids but higher volume fraction of particles shifts the flow behaviour to non-Newtonian. Particle size and size distribution are influenced by shear thickening behaviour of material which in terms depends on shear rate. At high shear rates shear thinning material resemble Newtonian fluid and at low shear rates shear thickening material resemble Newtonian flow. Pseudoplastics are shear thinning material in which long chain molecules of the system is believed to achieve a stable configuration through chain entanglement and molar cohesion. Thus high rate of shear decreases the apparent viscosity (shear stress/shear rate) which can be taken into account for spraying, brushing of paints. In PP/NBR blends; decrease in viscosity is evidenced by increase in shear rate. Dialtant is shear thinning materials where crystallization or structure formation occurs at high rate of shearing and thus the apparent viscosity of the system increases [30]. Polymer processing techniques such as extrusion, injection moulding requires high shear rates but finished part quality is often controlled by low shear rates. Complex fluids including polymer melts and solutions, block copolymers, polyelectrolytes, surfactants, suspensions,

emulsions etc. are non-Newtonian in nature. Modelling of these complex materials is characterized by testing the response of a material to large shear rate called as LAOS (Large Oscillatory Shear Flows). This technique records shear stress for large strain rate which is then modelled by using Fourier concepts. In most processing operations the deformations are large and rapid thus it exhibits nonlinear material properties. Thus to control the system response under this dynamic situation LAOS based modelling is very useful [31]. Shear rate is important as it can predict the miscibility of polymeric blend. A study reveals that microemulsion consists of a ternary blend of poly(ethyl ethylene) (PEE), poly(dimethyl siloxane) (PDMS) and a PEE-PDMS diblock copolymer exhibits Newtonian flow at low shear rates, at intermediate shear rates anisotropy in the morphology (leads towards shear thinning) is observed. Further increment in shear rate causes flow induced phase separation of blend and if shear rate is extremely high it resembles of immiscible blend [32]. Multicomponent polymer system scatters light under the influence of shear fields and the scattering mainly depends on shear rate. Rheo-optic technique uses electromagnetic radiation (optics) in studying the deformation and flow (rheology) of polymers with particular emphasis on polymeric solids [33]. Generally increment in strain rate results in decrement of ductility. But modulus and yield or tensile strength of a material increases with an increase of shear rate.

2.1.1.3 Flow Performance and Design

Flow behavior is an indirect measure of product consistency and quality as in industrial scaling operation batch to batch variation should be minimal. By tuning the processing conditions mainly temperature, strain rate and molecular composition wide ranges of molecular morphologies are possible, such as spherulitic, shish-kebab, or row-nucleated structures [29]. Prediction of flow performance while designing gives the scope that molecular morphology can be altered in desired ways. Flow behavior is an indirect measure of product consistency and quality and is responsive to properties such as molecular weight and molecular weight distribution. When the temperature of melt increases free volume around the polymer chain also increase which in turn facilitates easier flow. Complex structure of polymeric chain exhibits stronger effect of temperature on flow behaviour. Two types of flows are commonly studied for non-Newtonian fluids: simple shear and simple elongational (extensional) flow. Simple shear is uniform flow where each fluid element on same stream line undergoes same deformation and the distance between them remains unchanged. In extensional (or elongational) flow during processing, material undergoes stretching along the streamlines due to extensional deformation and the distance between particles on the same streamline changes. For industrially purposes Melt Flow Index (MFI) is carried out by the grams of polymer extrude per 10 min from a die of prescribed dimensions according to an ASTM standard under the action of a specified load. Melt flow index has direct correlation with molecular weight, density, viscosity, shear rate. Orientation of multi-component can be tailored to an external flow field viz. steady shear, extrusion, oscillatory. In modelling aspects

tensor coupled with course mesh size finite element calculation helps in prediction of planar flow and orientation. Flow analysis helps in obtaining in plane stiffness which helps in designing of complex shapes aided by computer based model. 3D micromechanical models for laminates like mould flow packages involves flow behaviour and prediction of mechanical properties [34]. Designers often use plasticizers, a high boiling liquid which works by lowering glass transition temperatures and improving the flow characteristics of the system.

2.1.1.4 Elasticity and Design

Elasticity is very useful in determining the mechanical properties of polymeric system especially in structural load bearing application. Polymers show excessive elastic deformation due to its inadequate stiffness. So, for controlling the failure of system designers play with elastic modulus of the material. Designers rely on factor of safety (ratio of ultimate stress to the actual stress) calculation for implementation of FRCs in structural application. For rubber processing elastomers are generally thermoplastic in nature which exhibits low modulus, elasticity at least twice of their original length at room temperature (when stretched) and has the ability to return to their approximate original length when stress is released. TPEs (thermoplastic elastomers) have the properties and performance of rubber, but they are processed like plastic. A thermoplastic elastomer has two segments viz. hard phase and a soft phase. Plastic properties of a thermoplastic elastomer are governed by the hard phase of the materials and soft phase of the material determines the elastic property. Behaviour of the hard phase is governed by processing temperatures, tensile strength, tear strength, peel strength, chemical and fluid resistance, adhesion to inks, adhesives, and over-molding substrates. Elastomeric property of the material is considered on the basis of lower service temperature limits, hardness, flexibility, compression set and tensile set.

Thus modulus of elasticity plays a vital role in designing this multi-component. Apart from thermoplastic elastomers, elasticity also influences designing of elastomeric alloys. Commercial elastomeric alloys are of two types melt-processable rubbers (MPRs) and thermoplastic vulcanizates (TPVs).

Resistance offered by polymer melt against stretching is termed as melt strength. It depends on the molecular chain entanglements of the polymer and its resistance to untangling under strain. Melt strength of the polymer is dependent on molecular weight, molecular weight distribution, and molecular branching. Increment of any property increases the melt strength. This relation is valid at low shear rates. In design aspects melt strength also affects in drawdown of extrusion coating. In co-extrusion process balance of melt strength can predict interfacial properties. Sometimes melt strength is related to the extensional viscosity of the polymer. A good elastic polymer material should have good damping properties and can be used in a variety of applications to absorb shock, dissipate heat, isolate vibration, or

damp noise. It should have a high damping coefficient, indicating that the material will bounce back or return energy to the system. It needs to be work in a wide range of temperatures and environments, including exposure to chemical.

2.1.1.5 Molecular Weight and Design

Molecular weight and its distribution is an important parameter in determining of material bulk properties. Generally high molecular weight permits higher degree of chain entanglement which in term associated with material high melting or softening temperature and high tensile strength. Failure or degradation of material is depicted as loss of material load bearing capacities. For example atactic polystyrene mechanical properties increases with increase in molecular weight below the glass transition temperature (T_g). Researchers correlated impact strength and toughness with molecular weight in glassy state of the material, impact strength increases with molecular weight. Fracture toughness is strongly dependent on molecular weight distribution [35].

Relationship between molecular structure and mechanical properties is very complicated. Evolution of excellent catalyst has minimized the effect of tacticity in high molecular weight polymers (isotacticity is maintained in commercial polymers). Flory proposed an empirical equation for predicting mechanical property by using molecular weight as an influential parameter.

$$P = A + B/M \quad (2.1)$$

where P stands for mechanical properties, M for molecular weight, and A, B are constants. A, B values are varied according to the property taken. If B is positive, mechanical properties decrease with increase of molecular weight and vice versa. Sometimes a more complicated empirical relationship is used where M is replaced by $M^2 + C$ [36]. Glass transition is another important parameter which is also dependent on molecular weight. An empirical expression relating the inverse relations between T_g (glass transition temperature) and $\overline{M}_n$ (number average molecular weight) is given by Blanchard et al. [37]

$$T_g = T_g^\infty - K/\overline{M}_n \quad (2.2)$$

where T_g^∞ is the T_g of an infinite polymer and k is an empirical constant. According to Flory-Fox glass transition temperature is the temperature where free space volume for molecular chain movement reaches its minimum value. In a polymer system chain end segments are restricted only at one end whereas internal segments constrained at both ends thus their mobility is more imparted than the end segments. As the number of chain ends increases (which means a decrease in $\overline{M}_n$) free volume increases thus T_g decreases. But in crosslinking intermolecular connection is

formed and this network structure results in increment of glass transition temperature. In broader aspects mechanical properties and resistance to chemical attack can be altered by molecular weight.

2.1.1.6 Chemical Changes and Design

Performance, durability and long term behavior of fiber reinforced composites for structural applications are tested under several environmental conditions. Simulated aggressive environments [38] are generally considered and the performance over a period of 6 months or more is monitored for a structural material. Generally performance of material is evaluated under neutral pH (fresh water); alkaline pH (saturated calcium hydroxide $\text{Ca}(\text{OH})_2$ solution (pH = 12.5)); acidic pH (hydrochloric acid, HCl, solution (pH = 2.5)). Apart from that material performances under simulated seawater, moist alkaline soil with microorganisms, UV radiation are sometimes also monitored. Simulated ocean water with a pH of 7.25 is used for simulating the marine environment. The major ingredients of this solution are NaCl (24.53 g/L), MgCl_2 (5.20 g/L), Na_2SO_4 (4.09 g/L), CaCl_2 (1.16 g/L), KCl (0.695 g/L), and NaHCO_3 (0.201 g/L) in water according to ASTM D1141. Chemical changes are considered as a performance indicator while designing for long term applications. Apart from that degradation studies (swelling and dissolution) are also taken into account while designing for end product disposal and recyclability (if possible) of the product. Degradation is basically a separation of chain segments—termed as scission. Scission effect or bond rupture can take place due to radiation effects, chemical reaction effects and thermal effects.

2.1.1.7 Physical State and Design

Temperature and pressure is the two main pillars controlling physical state of a material. Miscibility of most polymer-polymer system decreases with increase in temperature. Thermodynamic properties of polymer blend as a function of pressure and temperature are explained with the help of random phase approximation, self-consistent-field theory, and Flory—Huggins theory [39].

2.1.1.8 Other Parameters

Apart from the above mentioned parameters miscibility and phase separation and segregation also plays an important role while designing multicomponent system. Interfacial tension reduction, coalescence suppression, increase in compatibility are some approach towards obtaining miscible polymer blends.

Elastic modulus is a pressure dependent property of material. Increase in pressure decreases the free volume available in the structure and thus increases the modulus of elasticity. Ferroelectric polymers (from the polyvinylidene fluoride

(PVDF) family) exhibits piezoelectricity under mechanical stimulus. Mechanical stimulus causes change in the dipole densities and creates moderate piezoelectric coefficients in comparison to ceramic piezoelectric [40]. Piezoelectric materials are of three types.

- Bulk piezoelectric (molecular structure and orientation).
- Polymer piezoelectric composites (PVDF).
- Voided charged polymers [41].

In designing of shape memory polymer (SMP) physical state is an important parameter. To exhibit shape memory effect a material (generally elastomer) under thermal or other stimuli maintains the deformed state in a temperature region according to the relevance of the application [42].

2.1.2 Material Selection Approaches (Example) [43]

An example can be taken to explain the material selection approach for plastic material in medical device design:

Basics of polymers and their additives, properties, process-abilities are used to design the morphology of a multicomponent. Thoroughly defined applications are required to select appropriate candidate materials and careful consideration must be taken while combining different configuration. Final selection should be obtained by testing after narrowing of choices. Selection approach starts with-

1. Market trends and challenges, followed by
2. Design requirements in context of the application

Objectives of the material will vary from product to product and thus the features governing factor may not be the same for all material within the same classes also. As medical product requirement varies according to end application. Several tests are performed on the material according to the physical contact with human body which has been tabulated in table [1]. If floor panels of refrigerated trucks are considered than objectives varies accordingly, minimizing mass; minimizing cost; adequate thermal insulation to keep goods refrigerated and minimizing heat loss are the key objectives for this application. Likewise for medical products general objectives are to search on questionnaire basis (a selection strategy) on expertise advice considering several constraints.

Environmental constraints-

- Biocompatibility
- Contact ability (with body tissues or drugs-along with duration)
- Instrument/device usage-Single use/multi use
- Sterilization required or not (with frequency of sterilization)
- Reaction with other chemicals/solvent/vapours (ex. hospital cleaning)

- Attachment mode of device with body
- Exposure to humidity and temperature with time period (maximum and minimum)
- Dimensional stability under different condition
- Tolerances
- UV resistance (a requirement or not)
- Visibility under a fluoroscope or X-ray (a requirement or not)
- Flame retardability (a requirement or not)
- Colour of the material (If it is an influential parameter)
- Outdoor application (if any)

Dimensional and mechanical constraints:

- Parts dimensions (diameter, length, width, thickness)
- Load bearing capacity-time period-continuous or intermittent load
- Maximum stress on the part, kind of stress (tensile, flexural, etc.)
- Toughness or impact resistance-during application
- Wear properties
- Electrical insulator (if required or not)
- Available manufacturing processes
- Target cost of the component
- Projected life of the part or design
- other mechanical properties
- Static dissipation/conductivity/dielectric properties (if required)

3. Screening

- (a) Biocompatibility of the polymeric material is the first requirements for a material to be considered for medical device/biomedical uses.

According to application several types of polymers can be chosen-

Device/Instrument directly not connected with human body, e.g. syringes, blood storage bags, glucose drip bags (PVC, PA, PE, PS, Epoxy resins)

Device/Instrument in short period of contact with human body, e.g. catheters, feeding tubes, drainage tubes, surgical instruments (Silicone rubber, Natural rubber, PVC, Polyurethane, PE, PP, Polyester, PEEK, Polyphenylsulfone, Nylon, Teflon)

Device/Instrument in medium period of contact with human body, e.g. cultures, ligatures (Nylon, PP, Polyester)

Device/Instrument in long period of contact with human body, e.g. implants, drug delivery devices (PE, UHMWPE, PET, Silicone rubber,

Polyurethane, PMMA, Polysulphones, Hydrogels Polyphosphazenes, Thermoplastic elastomers, Polydimethylsiloxane)

- (b) Drug flow path (device performance under flow of drugs)
- (c) Chemical inertness, sterilization
- (d) Resistance to hospital cleaners (chemicals) against routine cleaning of devices
- (e) Mechanical properties
- (f) Electrical and Thermal Properties (dielectric strength and thermal resistance)
- (g) Dimensional stability, durability, aesthetics, radiopacity, conductivity, manufacturing feasibility

Finally correlation between technical performance and economics considering the screening tools:

Several biocompatibility tests are generally performed on polymeric medical devices before applications according to ISO 10993-1. Performance of the product is monitored under some common biological risks viz. cytotoxicity, sensitization, irritation, acute toxicity, sub chronic toxicity genotoxicity, implantation, hemocompatibility, chronic toxicity, carcinogenic, reproduction toxicity, biodegradation (Table 2.1).

4. Ranking of materials

A performance equation is used to determine the ranking of materials.

$P = [(F), (G), (P)]$ where F = Functional requirements, G = Geometrical parameters, P = Material properties.

Miniaturization, portability, improved aesthetics, and environmental responsibilities in medical devices have toughened selecting the right material with optimal product usability, appearance, endurance and performance. Sometimes pre-selection of material is also performed.

2.1.3 Case Studies

Tubular filament composite shaft designing [44]:

Specifications: Outside diameter-75 mm, inside diameter-55 mm, length of 1.0 m.

Main constraints: Bending stiffness (Strength, fatigue resistance is not significant since it is a filament composite). Maximum allowable deflection while subjected to a three point bending is specified as bending stiffness.

Problem: Load 900 N is to be applied at the center of the shaft producing a deflection not more than 0.3 mm. Continuous fibers parallel to the tube axis will be used in filament winding process. Possible fibers may be are glass, carbon in standard-, intermediate-, high-modulus grades, Kevlar with maximum allowable fiber volume fraction is to be 60%. Matrix material will be epoxy resin (Fig. 2.6 and Table 2.2).

Table 2.1 Selection of test for medical products as a function of contact method and time with human body [43]

Selection of tests for polymeric medical products ISO 10993-1										
Biological risks										
Cytotoxicity	Sensitization	Irritation	Acute toxicity	Sub chronic toxicity	Genotoxicity	Implantation	Hemocompatibility	Chronic toxicity	Cancerogenicity	Duration of contact
✓	✓	✓								Up to 24 h
✓	✓	✓								(>24 h-30 days)
✓	✓	✓								(>30 days)
✓	✓	✓								Up to 24 h
✓	✓	✓	*	*	*	*				(>24 h-30 days)
✓	✓	✓	*	✓	✓	*		*		(>30 days)
✓	✓	✓	*							Up to 24 h
✓	✓	✓	*	*	*	*				(>24 h-30 days)
✓	✓	✓	*	✓	✓	*		*		(>30 days)
✓	✓	✓	✓				✓			Up to 24 h
✓	✓	✓	✓	*			✓			(>24 h-30 days)
✓	✓	*	✓	✓	✓	*	✓	✓	✓	Up to 24 h
✓	✓	✓	*	*			✓			(>30 days)
✓	✓	✓	*	*						Up to 24 h
✓	✓	✓	*	*						(>24 h-30 days)
✓	✓	✓	*	*				*	✓	Up to 24 h
✓	✓	✓	*	*			✓			(>30 days)
✓	✓	✓	✓							Up to 24 h

✓Test to be included to ISO 10993-1
*Additional tests may be applicable

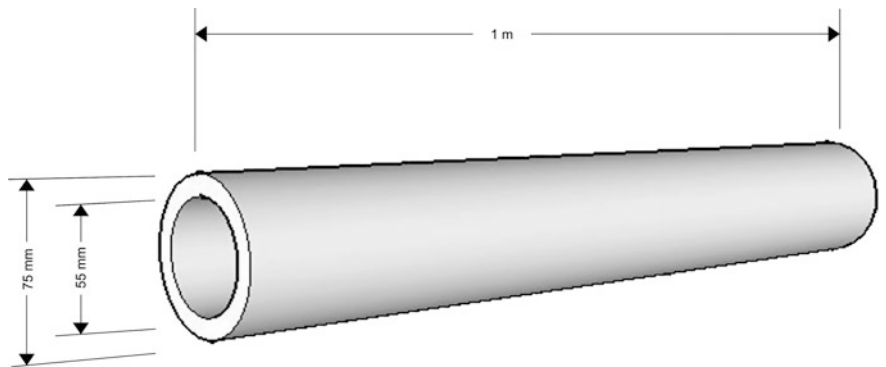


Fig. 2.6 Schematic representation of the drawing objective [44]

Table 2.2 Elastic modulus and density of different materials [44]

Material	Elastic modulus (GPa)	Density (g/cm ³)
Glass fibers	72.5	2.58
Carbon fibers (standard)	230	1.80
Carbon fibers (intermediate)	285	1.80
Carbon fibers (high modulus)	400	1.80
Kevlar	130	1.45
Epoxy	2.4	1.14

Solution: Three point deflection equation is given by $\Delta y = \frac{FL^3}{48EI}$ where F is the applied load, L is the gauge length, E is the modulus of elasticity and I is the moment of inertia (cross-sectional). So for computational necessities longitudinal modulus of elasticity is first needed to be calculated.

For a tubular shaft-

$$I = \frac{\pi}{64}(d_0^4 - d_i^4)$$
$$E = \frac{4FL^3}{3\pi\Delta y(d_0^4 - d_i^4)}$$

Following this problem F = 900 N; L = 1.0 m; Δy = 0.3 mm; d_0 = 75 mm; d_i = 55 mm.

Longitudinal modulus of elasticity is

$$E = \frac{4(900)(1.0)^3}{3\pi(0.3 \times 10^{-3})[(75 \times 10^{-3})^4 - (55 \times 10^{-3})^4]} \text{ GPa}$$

$$= 56.6 \text{ GPa}$$

In the next step fiber and matrix volume fractions are calculated for all potential candidates by using rule of mixtures.

$$E_c = E_m V_m + E_f V_f = E_m(1 - V_f) + E_f V_f$$

E_c is the modulus of elasticity of the composite and E_m , E_f are the modulus of elasticity of the matrix material and fiber respectively. V_m and V_f are the volume fractions of matrix material and fiber.

Taking $E_c = 56.6$ GPa respective volume fractions of different fibers are Tables 2.3, and 2.4.

From this chart it can be concluded that glass fiber cannot be chosen as maximum allowable volume fraction of fiber is 0.6.

So, after eliminating glass fibers from this design problem overall requirement of rest of the fibers and matrix for each composite type is necessary to be estimated.

Table 2.3 Volume fractions of matrix and fibers of the composites

Fiber type	V_m	V_f
Glass fibers	0.2268	0.7732
Carbon fibers (standard)	0.7619	0.2381
Carbon fibers (intermediate)	0.8082	0.1918
Carbon fibers (high modulus)	0.8637	0.1363
Kevlar	0.5752	0.4248

Table 2.4 Required weight of fiber and matrix in respect of a tube (designed)

Fiber type	Fiber volume (cm ³)	Fiber mass (Kg)	Matrix volume (cm ³)	Matrix mass (Kg)
Carbon fibers (standard)	486	0.875	1555	1.773
Carbon fibers (intermediate)	391.5	0.705	1649.5	1.88
Carbon fibers (high modulus)	278.2	0.5	1762.8	2.08
Kevlar	867	1.26	1174	1.338

Total tube volume

$$\begin{aligned}
 V_t &= \frac{\pi L}{4} (d_0^2 - d_i^2) \\
 &= \frac{\pi(100)}{4} (7.5^2 - 5.5^2) \text{ cm}^3 \\
 &= 2041 \text{ cm}^3
 \end{aligned}$$

In this design problem as strength and other design parameters are neglected the criterion for selecting an optimum material is purely based on economical. Assuming process cost of each type of composite remains same, total cost of each type of composite is considered (total cost including fiber and matrix) as selection rule. In general the cost of fibers and epoxy resin follows glass fibers < Epoxy resin < Carbon fibers (Standard) < Carbon fibers (Intermediate) < Kevlar < Carbon fibers (High modulus).

Again in design problem if performance of the shaft against twisting is considered than calculation regarding torsion needs to be estimated [45].

For tubular hollow composite shaft with a constant wall thickness, the torsion, T:

$$T = \frac{J}{r_0} \tau = T = \frac{J}{l} G \theta$$

where J is second moment of area given by

$$J = \frac{\pi}{2} (r_0^4 - r_i^4)$$

- τ maximum shear stress at the outer surface of shaft
- l gauge length of the tube
- r_i inner diameter of the tube
- r_o outer diameter of the tube
- θ angle of twist in radians
- G shear modulus or the modulus of rigidity.

2.2 Summary

Multi-component material designing is a function of constraints. The constraints are governed according to the performance of the material under certain environmental conditions and according to the end applications. Optimization and refinement in process defines the architecture of the material. Material selection is one of the main parameter while optimizing a process it basically includes evaluation of recent market trends and challenges; design requirements in context of the application;

screening and finally ranking of materials. Design of a material is influenced by several parameters like rheology, shear rate, flow performance, elasticity, molecular weight, chemical changes, and physical state of the material.

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