Design Manual Pt. 4.

Royal Ordnance Rocket
Motors.

Rocket Motors Division

DESIGN MANUAL

PART 4 - MATERIALS

ROYAL ORDNANCE
Defence systems, sub-systems and components

DESIGN MANUAL

PART 4 - MATERIALS

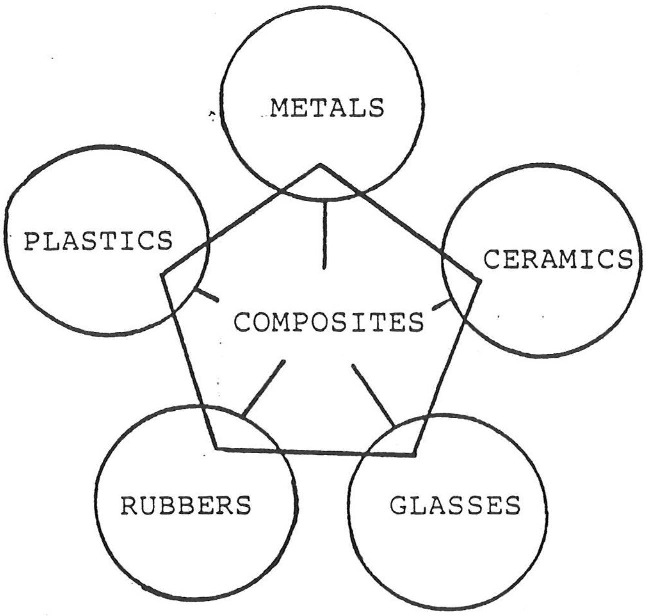
BY

DR D SIMS
MATERIALS MANAGER

MATERIALS

1. INTRODUCTION

Materials used in the construction of military equipment and rocket motors cover the full range from flexible rubbers to reinforced metals. The menu of engineering materials is illustrated below. Each class of materials has properties which occupy parts of a spectrum of stiffness, strength, density and these often overlap.



The procedures for selection and design are dependant on the material class. Processing techniques can often have very large effects on the mechanical properties of the final component and sometimes on the storage life. Thus, it is most sensible to discuss each class of material separately. It should be noted however that some materials, for instance thermoelastomers and self reinforcing polymers, fall into more than one category. Adhesives are covered in a separate section since these are commonly used to join both similar and dissimilar materials together.

A - THERMOPLASTICS

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1. SELECTION AND DESIGN

1.1 Need for Design

Although historically plastics usage has grown without it, the need for a coherent design and material selection methodology has long been recognised. Products must be engineered to fit them for their lives under stress in hostile environments. These stresses may arise as a result of the primary product requirements, for example, in a pressurized container, be encountered during transport or installation, or appear accidentally or as overloads (for example normal wear and tear in use).

The need for a systematic approach towards the engineering design of plastic components has often been by-passed by the "if in doubt, make it stout" method of specification. This is probably the main reason why many existing plastics products display little refinement in their design.

In recent years the increasing emphasis being placed on product reliability has brought new urgency to the problem. Plastics generally are substantially lower in strength and rigidity than the metals they compete with, especially at elevated temperatures. It has, therefore, become increasingly important to determine design allowable limits quantitatively under realistic environmental conditions. The major stimulus for the replacement of metals with plastics is cost, since many articles can be moulded to size with no post machining. The second is weight-saving since the specific gravity of many plastics is close to unity. In either case it has presented challenges for plastics designers to meet even more severe and complex loadbearing requirements. The development of plastics design technology has become important not just to the future of plastics, but also to the manufacturing industries that use them.

One major problem has contributed critically to the long delay in development of a coherent design and material selection technology for plastics. This is the profound difference between the viscoelasticity of plastics and the elasticity of structural metals in which the community of designers and product engineers has been primarily trained and upon which all of their analytical equations are based. When one considers the effect of viscoelasticity on properties, the dilemma becomes quite understandable. On the one hand, the designer has a network of design equations and relationships that call for certain material constants, such as yield stress, tangent modulus, and proportional limit derived from stress-strain tests. On the other hand, the designer finds that the results of such tests on plastics not only are not constants, but vary greatly with time under load, with rate of loading, with small changes in temperature, with method of production and even with details of testing. These properties do not have the significance for plastics that they do for structural metals and the designer is severely limited in the extent that he can use them in plastics design.

1.2 Logical Steps in Design and Development

To be coherent, the design and material selection technology which is required for plastics must do more than just identify performance properties and call out methods of testing for them. It must also provide a system for their use in the process of developing applications. The reasons for this lie in the complexity of plastics and the multiplicity of the applications. Firstly, plastics selection requires the consideration of many more different performance properties than the traditional materials they compete with, often because they are used in a much larger variety of applications. Frequently, the nature of plastics applications requires the compromising of a goodly number of these properties, including cost. Secondly, the types of stresses for which there are design equations and properties to substitute in them are relatively few, which forces us to depend heavily on properties that correlate in varying degress with performance. In fact, for some types of stresses, eg wear, adhesion, and impact, there are no material properties that reliably predict performance.

As a result of these complications, the material selection procedure for most plastics applications is rarely simple and should always be conducted in a very systematic way. It is particularly important to place in proper sequence the key steps for defining all requirements in applications terms and selecting valid material performance properties that reflect these requirements. It is also important to recognise the almost indispensible role of prototyping. What follows is a typical application development sequence that shows these steps in the proper context.

(1) Conception of the component, leading to an initial functional design, ie shape of the component and of its functional components, accompanied by selection of the basic fabrication process and appraisal of fabrication process on component properties. (Some input from a plastics expert may be useful here).

(2) Screening of candidate materials on the basis of processability and those engineering properties that relate to performance under the stresses that component functions impose on the material.

(3) Preliminary analytical design, ie calculation of wall thicknesses and other component dimensions using design properties where possible and experience where not.

(4) Prototyping and testing under actual or simulated component use including life tests to assess ageing.

(5) Redesign and retesting (and sometimes rescreening when overlooked properties turn up).

(6) Finalisation of design and material selection on the basis of prototype testing and fabricated component cost and material availability.

(7) Specification of selected material.

Sometimes these steps can be telescoped, especially where component requirements are simple or where the new part is only slightly different from older parts. On the other hand, the steps can become very complex, especially in new applications, or where the functional stresses are very challenging for plastics. In such cases, a systematic approach following this sequence is not only the surest route to success but is also the surest way of minimising development costs.

One of the most striking differences between plastics and metals arises in the selection of properties to be used in the material specifications. With metals, the same properties can be used for material screening, design, and specification, eg elastic modulus and yield stress. Not only do they predict performance but they are ideal for specification tests, that is, they are quick, easy and inexpensive. However, with plastics this is not the case. Plastics specification tests, usually the simple stress-strain properties and other A.S.T.M. or so-called single point data sheet properties, such as Deflection Temperature Under Load, Izod Impact, and the like, are not generally useful in predicting plastics performance. They are especially inadequate in judging long term behaviour and elevated temperature capability.

In all but simple applications, the proper philosophy with plastics is to rely on engineering properties and prototyping for materials selection and to set up the material specification afterwards to control the chosen material. In fact, this is the way most A.S.T.M. material specifications are written today.

1.3 Analysis of Part Function

This step consists of two distinct phases:-

(1) All the essential part functional requirements must be listed as quantitatively as possible in application terms, not material properties. Typical examples of requirements are:-

Maximum deflection of 0.25 mm at a given point under 25 Kgf continuous static load for say 5 years.

Maximum operating temperature 120 °C.

Maintain dimension between hole centres to ± 0.01 mm at operating temperatures for the life of the part.

Withstand impact of stones and other objects thrown up on the runway by an aircraft travelling at 120 mph.

Maintain part-to-part moulding consistency of ± 0.1 between specified dimensions.

Meet UL Std 94 flammability of V-2 in 1.5 mm thickness.

Resistant to ASTM Oil No 1.

(2) A target material profile must be developed by assigning values of design and performance properties which are required and which predict or correlate with the specific part functions derived in phase 1. The objective is a description of the required material as completely as possible by numerical values of meaningful material properties. Even when this can be done only approximately it greatly facilitates candidate screening and yields valuable insights into material selection.

Selection of the correct material properties is critical and often complex.

In some cases there will be no direct material property that relates to the part requirement, for example ablation. In such cases, the qualification of a material may have to be determined by trial and error or by numerical modelling.

1.4 Systematic Selection of Materials

The effective use of engineering properties depends mainly on the thorough and accurate completion of one critical step in the material selection process. That step is the analysis of the part or application functions in terms of the stress requirements they impose on the material and the translation of those requirements into material properties. In some cases a part requirement will be clear cut with respect to the type of stress imposed and the corresponding material property will be obvious. However, in most applications there usually will be functional requirements that are complex and will involve several stresses interacting in a complex way. Regardless of whether the functional requirements of the part are simple or complex, it is necessary for all of them to be taken into account and translated into performance-related properties for the material screening step to serve its purpose.

That purpose is to identify all the materials that can qualify for a given application. Material costs should not automatically be included at this stage. Although the goal ultimately is to find the material that can do the job at the lowest fabricated part or net cost, that cost is the end result of a series of factors that can interact in such a complex way as to cancel out differences in material cost per/cc. Examples of such factors are finishing, joining, productivity (cycle time, quality) design, stiffness, and strength. Frequently, the effect of these factors on net cost cannot be predicted without prototyping. In any case, the designer or product engineer should start by knowing all the materials that can satisfy the performance requirements of the application before beginning to work out the ultimate cost-effective selection. It is also useful not to be tied to a single source material if at all possible.

1.5 Screening Candidate Materials

A quick glance at any book on plastics shows that there are more than 30 basic commercial materials subdivided into many thousands of grades. It is important not to be confused by the designation "engineering plastic" since virtually all unfilled plastics have a short term modulus between 1 and 3 Gpa. What appears to constitute an engineering plastic is one of higher service temperature, ie above 100 °C. Most low stiffness materials can be made much stiffer by the incorporation of glass or carbon fibre which also increases their upper use temperature.

Manufacturers lists, catalogues, handbooks and computerised search lists are available for the selection of materials but, as with other materials, the information contained in these lists is of undefined accuracy and often from different test methods. Information falls into two groups firstly the single point data which are suitable for preliminary material class selection purposes then multipoint data which help decide the grade within a class.

(a) Single-point data

Density
Water absorption
Glass content/other fillers
Hardness
Deflection temperature under stress
Vicat softening point
Thermal expansion
Mould shrinkage
Thermal conductivity
Specific heat
Flammability
Oxygen index
Dissipation factor
Permittivity
Volume resistivity
Surface resistivity
Electrical strength
Comparative tracking index
Flexural modulus
Flexural strength
Tensile modulus
Tensile strength
Elongation to break
Impact strength, Izod and Charpy

(b) Multipoint data

Tensile strength
Flexural strength
Creep rupture
Tensile creep modulus
Poisson's ratio
Flexural creep modulus
Dynamic shear modulus
Shear loss factor
Charpy impact strength
Environmental stress cracking, tensile
Environmental stress cracking, flexural
Chemical resistance
Thermal resistance
Linear expansion coefficient
Specific heat (DSC method)
Volume resistivity
Dielectric constant
Dielectric loss factor
Electric strength
Viscosity of melt

At this point designers are recommended to consult a plastics materials expert to interpret and understand the mass of data available.

1.6 Engineering Data

The basic problem with all thermoplastics is that they show different responses to stress from metals. In some situations they can be treated as traditional materials with appropriate effective values for Young's modulus and Poisson's ratio but more normally for long term applications they cannot.

A schematic stress strain curve for metals and plastics is shown in Figure 1. (Note the different strain axes for metal and plastics).

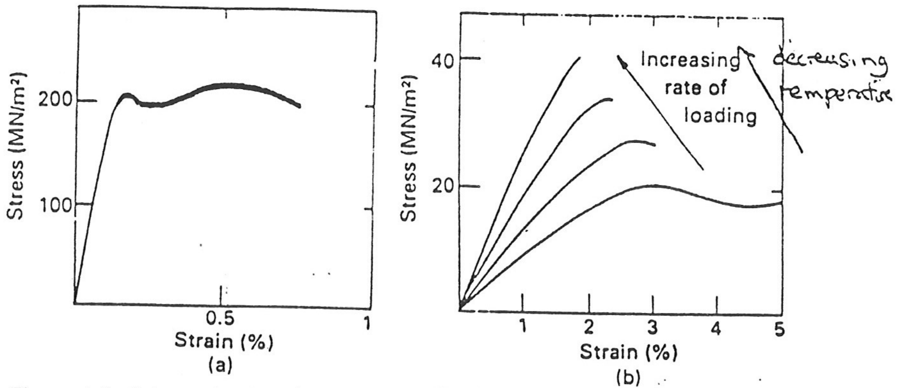


Figure 1.1 *Schematic stress/strain curves for (a) metal and (b) plastics. Axes indicate orders of magnitude.*

The significant feature is that plastics do not show a unique stress strain curve but a set of curves dependent on rate or frequency of loading and temperature. This behaviour arises from the viscoelastic nature of plastics materials whereby the response to a steady stress is a small elastic strain followed by a significant creep component.

Thus the apparent modulus decreases with time of application of load. Standard methods of calculating design stresses rely on information about modulus and/or yield stress but for plastics these are multivalued. With enough information about loading history and elapsed time, a standard design formula can be used.

Even in a simple loading situation where creep curves are available, these can be insufficient on their own, since other non quantifiable factors can arise, such as:-

(1) fluctuations in service stress.

(2) stress system will seldom be simple.

(3) most mouldings are anisotropic.

These effects are difficult to deal with and in most cases have to be accommodated by de rating factors.

The designer is recommended to consult an expert text on methods of approximate design.

1.7 Additonal Requirements

Strength and rigidity are not the only areas where the designer of plastic parts needs design and performance data. Development of a plastic application usually requires compromising with other properties in addition to mechanical, such as heat-ageing resistance, electrical properties, optical clarity, effect of organic and other liquids, permeability, flammability and processibility. Included for many RO applications is also compatibility with explosives and propellants. Because of the diversity of applications and the frequent occurrence of multifunctional parts, even fairly simple applications of plastics present a significantly more complex property mix than most metal parts.

Ageing and the effects of moulded-in stress are particularly difficult areas for designers to deal with and in most cases expert advice should be sought. Ageing can result in a large decrease in retained properties without necessarily any visual changes occuring.

Moulded-in stress can result in slow irreversible warpage such that intermeshing parts will no longer function. This effect is over and above any creep due to continuous loading and is often triggered by short term exposure to high temperatures.

1.8 Plastics Material Properties

The following section is only intended to give a very brief outline of the advantageous characteristics of individual classes of plastics. It is not intended as a selector for materials.

1.8.1 Acetals (POM)

Acetals are polymers and copolymers of formaldehyde. They are strong tough rigid crystalline materials with excellent dimensional stability and low moisture absorption. Their coefficients of friction are low and abrasion resistance excellent throughout the range. Fatigue endurance is good and chemical resistance to most organic solvents excellent. However strong acids and alkalis attack acetal and they are also affected by prolonged hot moist conditions and sunlight. The effects of sunlight can be greatly reduced but not eliminated by the incorporation of carbon black.

Major uses of acetals are in bearings, bustings, gears, housings, pumps and electric motor parts.

1.8.2 Acrylics (PMMA)

The combination of three properties distinguishes acrylics from other plastics materials. These are:-

(1) Excellent transparency with optical clarity.

(2) Exceptional stability to weathering and discoloration by ultraviolet radiation.

(3) Extremely hard, easily formed by heat and easy to decorate.

Acrylics occur as two types, first the high molecular weight cast sheet, block or rod material and the moulding grades. The properties have led to wide use of the material for glazing, aircraft canopies, light fittings, reflectors, lenses and consumer durables. It should not be overlooked however that acrylics like many plastics are readily combustible.

Although acrylics are one of the hardest plastics they are rather notch sensitive and show low resistance to many common organic solvents.

1.8.3 Acrylonitrile butadiene styrene (ABS)

ABS and similar materials such as MBS and AAS have an exceptional balance of properties which makes them very useful for consumer durables. ABS shows very high impact strength, high gloss, easy mouldability with low shrinkage and reasonable temperature resistance. It is extensively used for fridge liners, toys, instrument bodies including telephones and metal platable grades are readily available.

The main limitation to these materials is their poor weathering behaviour and their lack of resistance to chlorinated and other polar solvents.

1.8.4 Cellulosics (CA, CAB, EC)

These materials are derivitives of natural cellulose and represent the earliest known polymers. Nitrocellulose is now little used except in propellants but cellulose acetate is used for photographic film and cellulose acetate/butyrate (CAB) has a small market for moulded goods. Ethyl cellulose is used mainly in a protective film formulation for tools and is known for its low temperature toughness. All cellulosic polymers need plasticisers to be useful and generally their market share is declining.

1.8.5 Fluorocarbons (PTFE)

The most important member of this class of materials is polytetrafluroethylene (PTFE). However this material can only be fabricated by sintering and efforts have been made to produce mouldable materials without losing many of the unique properties of PTFE. These latter materials include TFE, FEP, PCTFE, PVDF and other copolymers. The major properties of PTFE are chemical inertness and the lowest coefficient of friction of any known solid material. It also has good electrical properties and very low permittivity and power factor. However PTFE has relatively poor mechanical characteristics. It shows high creep low resistance to wear and poor dimensional stability which can be overcome to some extent with fillers. It is also very expensive. PTFE can be used over a temperature range of - 250 to + 260 °C and remains ductile to about - 200 °C.

1.8.6 Polyamides (PA)

Polyamides, or as they are more commonly known nylons, are in common use. There are many possible materials their chemical composition being designated by number ie nylon 66, 6, 6.10, 11, 12 and 13. Of these the bulk of production is in nylon 66, 6 and 11 although nylon 12 is now becoming more common.

Although all nylons have properties common to the generic group such as oil resistance, each type has some properties specific to the type. Nylons 6 and 66 together with their glass filled grades are general purpose engineering materials. The remainder find application when specific properties ie lower water pickup is required. All nylons are hygroscopic and the amount of water absorbed has a profound effect on their mechanical and electrical properties and on the dimensions of articles made from nylon. The maximum water content ranges from 9% for nylon 6 to 2% for nylons 11-13.

However in the UK with a relative humidity of some 65% rh. the amount absorbed at equilibrum is about 1/3 this value. It also takes a long time for the absorbtion to reach equilibrum values at room temperature typically 300 days, therefore humidification may need to be accelerated by boiling nylon articles in water whereby the period is reduced to a few hours for a 3 mm thick section. Unstabilised nylons are also sensitive to oxidative degradation above 70 °C. However, suitable stabilising systems are available to allow continuous service in excess of 100 °C. Uses of nylon include gears, bearings, housings, electric motor and drill housings, air and hydraulic lines.

1.8.7 Polycarbonate (PC)

Polycarbonate is one of the newer engineering thermoplastics. It is transparent, extremely tough, has good dimensional stability and a wide temperature range of use. The basic material does not support combustion. This combination of properties has opened up a market in light fittings, car fitments, lenses, vandal proof fittings and bank screens. Polycarbonate has moderate weathering resistance in stabilised grades but is sensitive to certain solvents in particular esters, ketones and aromatic or chlorinated hydrocarbons.

1.8.8 Polyethylenes (PE)

Polyethylene as one of the oldest thermoplastics needs little introduction. However many different types are now available. The earliest grade was low density polyethylene, LDPE, (density 0.918 - 0.930 g/cc) discovered by ICI in 1933. This is a relatively soft material showing a broad melting band from about 95 °C to 125 °C. High density polyethylene, (HDPE) was discovered in the 1950's and is more crystalline thus harder with a sharper melting point and higher density (0.95 - 0.96 g/cc). Intermediate grades are also available. Within the last year linear low density polyethylene (LLDPE) has emerged. This is really a copolymer of ethylene with another diene such as butene-1. The incorporation of a small amount of butene allows retention of many of the favourable properties of LDPE but increases puncture and tear resistance of blown films and bottles.

Polyethylene is widely used in film, coatings, housewares, crates, dustbins, bottles, pipe and sheet.

1.8.9 Thermoplastic polyesters (TPE)

Thermoplastic polyesters have been known for many years and one particular member of this family, polyethylene terephthalate spun into fibres under the trade name Terylene has been extremely successful. What has held back these materials as moulding compounds has been control of crystallinity. Both crystalline and amorphous grades of thermoplastics polyesters are now available but the crystalline grades have found most use. The materials are very hard strong and ductile with low friction, low wear, good electrical properties and very low water uptake. The upper use temperature is about 130 ^{o}C although a small transition at 80 ^{o}C can cause some dimensional problems. Chemical resistance is generally good but prolonged contact with steam degrades the material. Uses are in electrical components and underbonnet car applications.

1.8.10 Polyphenylene oxide (PPO)

Although known as PPO the material generally available is a polyphenylene oxide polystyrene blend (Noryl). The material is very similar to ABS with an excellent balance of properties. Creep is low, impact strength is retained to about - 40 ^{o}C and Noryl black grades are more resistant to weathering than ABS. Noryl is also resistant to nitroglycerine and oxygen gas. Applications include office machinery bodies, domestic appliances antomotive parts and military components.

1.8.11 Polypropylene (PP)

The route to polypropylene was discovered at about the same time as high pressure polyethylene and the two materials compete for many applications. Polypropylene is one of the lightest thermoplastics (density 0.91 g/cc) and is more rigid than the polyethylenes. It is free from environmental stress cracking sometimes shown by polyethylenes in contact with detergents. Polypropylene has lower impact resistance than polyethylene but copolymers with ethylenes are now available with better performance. It is also more susceptible to attack by ultra violet light but suitable stabilisation systems are available. Polypropylene is also susceptible to contact with some metals including copper and titanium. Nevertheless after polyethylenes, polypropylene has a significant market share being used in many consumer durables, fans, washing machine tubs, furniture, stadium seating, luggage and crates.

1.8.12 Polystyrene and copolymers (PS)

Polystyrene polymers are still very important ranking third in world consumption after polyethylene and PVC. Styrene is easy to process by all conventional techniques. The base material is transparent and rather brittle but many copolymers are available with for instance acrylontrile (SAN), butadiene (toughened polystyrene, TPS) and both of these to give ABS described earlier.

The largest market for polystyrene and TPS is in vending cups and other one trip disposibles.

Polystyrene is easily converted to a foam by incorporation of a volatile blowing agent into the polymer bead. Expanded polystyrene can be blown to densities as low as 16 Kg/m^3. (1 lb/cuft). Because styrene and its copolymers are hard and glossy and can be easily coloured a significant market is in toys.

Polystyrene as an engineering material has a number of disadvantages. The unmodified crystal grades are rather brittle have a low softening point and burn giving copious black smoke. The modified grades whilst having better impact behaviour do not weather well and all are susceptible to organic solvents.

1.8.13 Polysulphones (PSU, PES)

These are a family of rigid, ductile, high strength, high temperature thermoplastics which maintain their properties from - 100 °C to above 150 °C. The normal unreinforced materials are transparent yellow to amber, will not support combustion and give off almost no smoke.

The electrical properties of the materials are excellent allowing use as high temperature connectors.

Polyether sulphone has better high temperature performance than polysulphone and can be used for thousands of hours at 200 °C without significant loss of strength. Being amorphous the polysulphones show outstanding creep resistance and have low coefficients of expansion. Their impact strengths are similar to polycarbonate but like polycarbonate are sensitive to notches, sharp corners and some chlorinated and polar solvents.

Present uses include high temperature electrical components, bearing cages and aerospace components including missile nose cones and radomes.

1.8.14 Polyphenylene sulphide (PPS)

Polyphenylene sulphide is one of another relatively new family of engineering polymers characterised by high thermal stability and outstanding chemical resistance. There are no known solvents for PPS below 200 °C. Polyphenylene sulphide shows high compatability with a number of fillers which can be used to modify the properties and hardness of the base material.

The properties of the material suggest uses in electronic components, carburettors, corrosion resistant parts and antifriction coatings. The growing use of ABS braking systems on cars allow use of PPS as hydraulic fluid resistant mouldings.

1.8.15 Polyvinyl chloride (PVC)

PVC is the most widely used of all thermoplastics. PVC resin as produced is a white rather intractible powder of little use alone but when blended with stabliser, plasticisers and lubricants which make the compound processible a whole range of compounds of various properties are possible. PVC with low or no plasticiser is rigid and tough and is widely used in buildings for sheeting, drainpipes and gutters.

The softer flexible compounds are used for cable insulation, film, hosepipes and as coated textiles.

The main attributes of rigid PVC are cheapness, low flamability, resistance to chemical attack and good weatherability. Disadvantages are limited temperature range - 10 to + 70 °C and the flammability of most soft highly plasticised grades.

1.8.16 Other Engineering Polymers

The last ten years has seen the introduction of other engineering polymers with high strength and toughness and high continuous use temperature. All of these materials are aimed at specific high temperature uses and they are all relatively expensive.

This group includes PEEK and PEK from ICI, PEI from General Electric, thermoplastic polyimides froma number of manufacturers and very recently the liquid crystal reinforced thermoplastics such as ICI's SRP material. In addition many blends are appearing which combine properties from two or more classes of material.

2. FABRICATION TECHNIQUES

What follows is a summary of the principal techniques available for the processing of thermoplastics.

2.1 Blow Moulding, Extrusion, Injection, and Stretch

Extrusion blow moulding consists of closing a mould around an extruded, hollow molten polymer "ingot". High pressure air is then injected into the centre of the hollow causing the polymer to expand against the surfaces of the mould.

The technique can be intermittent or continuous depending on the size and shape of the component. Examples of the process are the new 2 litre carbonated drinks containers.

Injection blow moulding involves two stages, the first of which is formation of the polymer "ingot" in a preform cavity. The "ingot" is then transferred to the blow mould where again high pressure air expands the polymer to the shape of the mould. Examples of this process include drugs containers up to 12 oz in size.

Stretch blow moulding consists of stretching, either mechanically or otherwise, a polymer "ingot", which has been formed by either extrusion or injection moulding. During the stretching operation high pressure air is applied in both axial and radial direction. In applying air in the two directions the molecules are aligned along two planes.

The major advantage of blow moulding, in general, is a fast rate of production.

The injection blow moulding process offers many advantages over the extrusion technique in the following respects:-

(1) It produces scrap-free, close tolerance, completely finished containers that require no secondary operations.

(2) It offers positive weight control in the finished container. (Accurate to within ± 0.1 g).

(3) Neck shapes and finishes, internally and externally, can be moulded with an accuracy of ± 0.1 mm.

(4) Repeatable weight and container dimensions possible with the process allow for compatibility and ease of operation in conjunction with filling lines.

(5) There is some amount of biaxial orientation which leads to an increase in strength of containers.

(6) Minimum operator supervision is required.

The stretch blow moulding process offers the following advantages over the other processes:-

(1) A greater amount of biaxial orientation allows improved strength, particularly with respect to impact strength, gas and moisture permeability, and stiffness.

(2) As a result of strength increases savings in resin can amount to 40% over the extrusion and injection processes.

The major disadvantage of the injection blow moulding process over extrusion and stretch blow moulding is in the size of component which can be produced.

2.2 Casting of Thermoplastics

Castings may be made by pouring monomers or partially polymerised syrups into suitably designed moulds and heating to complete the polymerisation.

When applied to tube production the monomer or syrup is poured into a metal mould. The mould rotates in a heated water bath and the centrifugal effect forces the material against the wall where it polymerises. Wall thickness is controlled by the amount of material, the heating cycle, and the spinning rate.

The advantage of the system is that tubes with outside diameters from 30 to 600 mm and wall thicknesses of 2 to 15 mm with lengths up to 2 m can be produced.

The disadvantages of the system include:-

(1) High shrinkage in the mould.

(2) Increase in temperature during the reaction may cause explosions.

(3) A post cure, when moulding is complete, may be required.

(4) Possible thermal degradation due to material being heated for a relatively long period.

(5) Slowness.

2.3 Extrusion

Extrusion is a major production process for rod, tube sheet and profiles. The extrusion process may be defined as the forcing of molten polymer, under pressure, through a shaping die. For tube production the die design is tailored to the final shape desired. Most tube profile shapes are sized by applying cooling and vacuum similtaneously in a suitable fixture located at the entrance to a sealed cooling bath. Internal air pressure or external vacuum is maintained in the tube, until it is sufficiently cool, to keep its roundness. The main advantage of the system is the fast production rate, the disadvantage being that dimension tolerances are not very easy to control. Extrusion of filled thermoplastics is very difficult.

2.4 Foam Processing. Expandable Moulding, Extrusion, Melt-Processable Moulding, Multi-Component Liquid Foam Processing

The expandable moulding of foams is applicable, in the main, to polystyrene. There are three broad catagories of expandable moulding, these are block moulding, custom moulding, and cup moulding.

All of the techniques involve the use of polystyrene beads which contain blowing agents. The raw material is expanded to the desired bulk density of the end use article, is aged or conditioned, and then moulded.

The extrusion of thermoplastic foams is accomplished by the thorough mixing of a gas-forming blowing agent into the polymer melt and subsequent extrusion under carefully controlled conditions.

Melt-processable structural foam is a thermoplastic polymer with an integral solid skin, surrounding a cellular or foamed core. Structural foam parts are manufactured using methods similar to conventional injection moulding; foaming, however is achieved through the addition of a blowing agent.

Multicomponent liquid foam processing involves pouring or injecting a chemical mixture into a mould where it reacts to fill the cavity with a thermosetting cellular plastic.

The advantages of foam processing are:-

(1) Fast cycle times.

(2) The production of structural foams by the melt-process, this means that a low density high strength component can be produced.

(3) All thermosetting polymers can be foamed, so the polymer chosen can be based on the property requirements of a system.

2.5 Injection Moulding of Thermoplastics

Injection moulding is the most widely used production process for thermoplastics materials. The injection moulding process involves the melting or plasticising of a plastic in pellet or powder form and the injection of this melt into a mould which is held closed by a clamping mechanism.

Co-injection moulding, or sandwich moulding as it is sometimes called, is a process which permits injection moulding of parts with a skin of one thermoplastic and a core of another compatible thermoplastic. Most commonly, the skin material is solid whilst the core material contains a blowing agent.

The advantages of injection moulding processes definitely lie with the speed and control of production, coupled with the minimum of labour required for the processess.

The advantage of co-injection moulding over conventional structural foam moulding is that secondary surface operations are reduced and with the foamed core the parts are stress free and offer high dimensional stability.

2.6 Reaction Injection Moulding

This moulding technique is a relatively new process that involves simultaneous high pressure injection of two or more reactive liquid streams into a mixing chamber followed by low pressure injection into a mould cavity. Its main use is in the production of structural foam products. The material produced by the process is characterised by light weight and rigidity.

2.7 Rotational Moulding

The basic rotational moulding process is simple; a solid or liquid polymer is placed in a mould, the mould is first heated then cooled whilst being rotated about two perpendicular axes simultaneously. During the first portion of the heating stage, when moulding powdered material, a porous skin is formed on the mould surface. This gradually melts as the cycle progresses to form a homogeneous layer of uniform thickness. When moulding a liquid material, it flows and coats the mould surface until the gel temperature of the resin is reached, at which time all flow ceases. The mould is then moved to a cooling station where forced air and/or water spray cool the mould.

The main advantages of the process include:-

(1) Unlimited product design freedom.

(2) Machinery cost is low relative to production capability.

(3) Complex parts can be moulded without the need for part assembly.

(4) Parts are manufactured with very little stress because pressure is not required.

(5) Added strength in the corners and uniform walls are an inherent part of the process.

(6) For impact strength and stiffness, parts can have a multilayer construction.

(7) Double walled items can be produced.

2.8 Vacuum Forming

With vacuum forming a sheet of plastics material is heated, usually by radiant infra red heaters, then pulled down by vacuum into a female cavity or over a male former. Better thickness control can be obtained by first blowing the sheet up into a bubble and then forming over the former. The process is most suited to large flattish shapes such as covers, canopies, trays etc.

3. STANDARDS FOR PLASTICS MOULDINGS

For many years specifications have existed for plastics moulding materials, but only a few have been produced to control the quality of plastics mouldings. Some of the existing specifications for mouldings have been for general use while many have referred to the manufacture of particular defence stores.

Some Defence Standards have also been issued for plastics mouldings from the most widely used materials and these contain all the necessary technical information to control the quality of these mouldings.

3.1 Part Design

To avoid undesirable features in mouldings it is important that the moulding cycle, part design and mould design be carefully chosen and controlled. Principal defects and undesirable features are described below.

3.1.1 Low Strength

(1) When a thermoplastics material is moulded it is subjected to heat and pressure. If the dwell time is excessive and air or, in some cases, moisture is present, the material may be degraded resulting in loss of strength.

(2) An incorrect choice of gate design and location may result in low strength in certain parts of a moulding. This is particularly so with some materials which are reinforced with long fibres.

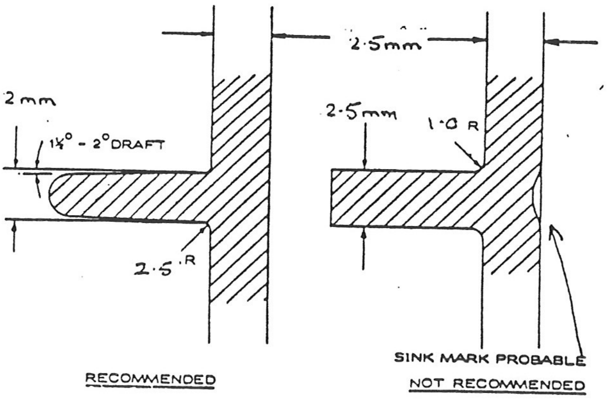
(3) The mechanical properties of fibre filled plastics mouldings are critically dependent on fibre length, distribution and orientation. In the injection moulding process excessive reduction of fibre length is caused by incorrect moulding conditions, whilst fibre distribution and orientation are mainly dependent upon mould/component design.

3.1.2 Surface Effects

(1) Where surface finish is important the mould must be designed so as to avoid marks due to gates, ejector pins, flow around bosses or ribs and split lines.

(2) Large, flat areas are always prone to warpage, which may be reduced by mould design and/or ribs on the moulding. Mouldings containing rapid changes in cross sectional area may exhibit sink marks, internal stress or cracking caused by differential shrinkage. Figure 2 shows the recommended use of ribs.

Fig.2



3.1.3 Thick Sections and Mould Shrinkage

Shrinkage is defined as the difference between the corresponding linear dimension of the mould and the moulded piece both measured at room temperature. This can vary from 0.1 to 1.5% dependant on material.

As an article is taken from the mould, thin sections cool more rapidly than thick ones and the thick sections tend to shrink more thus generating internal stresses. If the section exceeds about 10 mm, internal voids may also form. On large, flat sections internal ribs are necessary to minimise warpage.

3.1.4 Sharp Corners

Many plastics are very notch sensitive therefore internal corners should be given the biggest possible radii in relationship to the wall thickness. Figure 3 shows the effectiveness of fillets in reducing stress concentrations at a change of wall thickness.

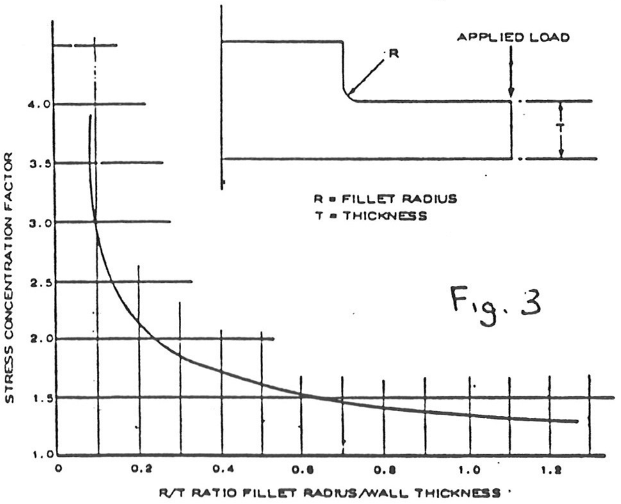


Fig. 3

3.1.5 Taper or Draft

It is often overlooked that it can be difficult to remove a parallel sided moulding from a cavity or off a core and provision should be made wherever possible for a draft angle on both outside and inside of a product. Tapers of 1 ° are suitable but in certain cases smaller values are acceptable.

3.1.6 Undercuts

Articles must be capable of being removed from the mould after they are formed. This point is frequently overlooked and parts are often designed with undercuts which make direct ejection difficult. Undercuts require split moulds or collapsible cores which are both expensive and unreliable in operation so they should be avoided if at all possible.

3.1.7 Holes

For a variety of reasons holes are often required in a moulding. Holes introduce weakness for two reasons. Firstly they are stress raisers; secondly material must flow around the projection forming the hole and the two flows rejoin, thus giving a weld line which may be much weaker than the surrounding material.

The problem is more complicated with threaded holes because of notch sensitivity.

In general the distance between successive holes or between a hole and the sidewall must be at least equal to the diameter of the hole.

3.2 Quality Assurance Tests

Apart from normal dimensional checks and visual examinations to confirm freedom from imperfections, cracks, blisters and contamination, etc, mouldings may be subjected to the following tests.

3.2.1 Density

Measurement of density and comparison with the nominal value establishes that the mouldings are reasonably free from porosity.

3.2.2 Chemical Requirements

These tests confirm that the concentration of impurities such as phenols, formaldehyde, lead and ammonium compounds, chloride and sulphate, which may sensitise explosives or promote the corrosion of nearby metallic components, are kept to an acceptably low level.

3.2.3 Dimensional Stability

If the dimensions of a component are critical then a dimensional stability test is needed to determine whether the dimensional requirements of the mouldings are retained during long term storage or use.

Changes in dimension are determined after heating the moulding at a specified temperature for a prescribed period and measuring the deformation on cooling.

For components moulded from a hygroscopic material such as nylon, the dimensional stability test is conducted on mouldings in the "dry" as-moulded state.

This test does not take into account possible dimensional changes arising during use from changes in temperature or absorption of moisture.

3.2.4 Freedom from Residual Stress

The residual stress within the moulding may give rise, in time, to stress cracking, and additionally, to the undesirable dimensional changes mentioned above.

One method of assessment of residual stress in certain thermoplastics is to immerse the moulding in a standard stress cracking agent at a controlled temperature and to observe the extent of the cracking or crazing. Mouldings which have unacceptable surface stress levels show widespread or severe cracking and/or crazing, and the batch they represent may be unacceptable.

3.2.5 Solution Viscosity

Chemical and thermal degradation can occur during processing with resultant reduction in molecular weight and loss of physical properties. In some cases degradation may cause darkening in colour but is more accurately assessed for thermoplastics by comparing the viscosity of a dilute solution of a representative part of the moulding with that of a similar solution of the moulding granules used.

3.2.6 Resistance to Low Temperatures

Many plastics have high coefficients of expansion and also become brittle at low temperatures. The test is intended primarily for use with mouldings with metal inserts and to assess the extent of cracking, if any, that will occur due to the differential thermal contraction between inserts and plastics, when mouldings are subjected to low temperatures without thermal shock.

3.3 Responsibility of the Designer

In addition to the normal engineering requirements such as dimensional tolerances, the designer will need to define the quality required by stating special requirements on the drawing.

These requirements include:-

(1) The specification, type, and the colour of the moulding material, together with the specification for mouldings in this material (if issued) and where necessary the manufacturing process to be used eg compression, injection, or transfer moulding.

(2) Any limitations on mould design, such as position of gate, flash, or pin marks which could affect the properties, assembly, or operation of the component.

(3) Details of inserts, if any.

(4) The positions, dimensions, and details of identification marks.

(5) Post moulding treatments such as annealing, or post-curing, if any.

(6) The maximum size and location of acceptable voids. For some non-critical applications the designer may be able to specify the maximum size and location of voids which will not impair the operation of the moulding in service.

(7) A dimensional stability requirement. If the dimensions of a moulding are critical, and are required to be within the drawing tolerances throughout the life of the component, the designer can invoke a dimensional stability requirement. The designer must note on the drawing special tolerances for any critical dimensions, to which the moulding must conform after being subjected to an accelerated test at an elevated temperature. When quoting tolerances, the designer must bear in mind that a moulding may undergo additional dimensional changes in use due to temperature changes and moisture absorption.

(8) A low temperature resistance requirement, to confirm that mouldings, particularly those with metal inserts, have adequate resistance to cracking at low temperature.

(9) Any requirement for mechanical tests on the component or samples cut from the component.

(10) Special requirements such as resistance to fire, electrical tests, special tests for filled materials or compatability requirements.

(11) Any special storage requirements.

(12) For moisture sensitive materials, the equilibrium water content of the mouldings.

3.4 Responsibility of the Manufacturer

Since the physical and mechanical properties of plastics mouldings can be adversely affected by incorrect mould design and incorrect moulding conditions, it is essential that manufacture is carefully controlled. It may be necessary for the Design Authority to approve a mould design for critical parts. Before allowing bulk manufacture a contractor should be required to establish moulding procedures acceptable to the Quality Assurance Authority. After first-off mouldings have been declared acceptable the moulding procedure shall be controlled and records of all procedures and machine settings must be retained during bulk manufacture.

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B - RUBBERS

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1. INTRODUCTION

Vulcanized rubber, in all its various shapes and forms, is widely used in engineering applications. Rubber is unique in its ability, unlike other engineering materials, to undergo large elastic deformations without rupture and to recover almost completely after such deformation. These elastic deformations can be in tension, compression, shear or torsion, although in practice it is advantageous to avoid tensile conditions particularly with intermittent loading conditions.

Initially the only rubber polymer available was that produced from tree latex, ie natural rubber, but since the 1930's there has been tremendous activity in the polymer field, with the development of a large number of synthetic rubber polymers. This vast increase in the number of rubber polymers available has greatly increased the complexity of choice of suitable materials.

To make it of practical use, rubber has to be subjected to a chemical reaction known as vulcanization, a process discovered by Goodyear in 1839. He found that when raw rubber was mixed with sulphur and heated, the doughlike mixture was converted to an elastic material that is generally referred to simply as "rubber".

Nowadays many diverse chemicals are used in producing a rubber and the inherent properties can be varied over a wide range by differences in compounding to produce an infinite range of possible rubber materials. Ingredients added fall into two classes, those essential to the production of the correct vulcanizate and those used mainly to cut the cost of the end product. The essential ingredients include the vulcanization system, fillers which impart specific properties and antidegradants.

Vulcanization, or the curing process is generally carried out under pressure in metal moulds at temperatures of at least 140 $^{\circ}$C.

2. SELECTION AND DESIGN

2.1 Logical Steps in Design

Rubbers can be compounded such that a given set of simple mechanical property requirements can be met by a large number of possible compounds. However there are many deficiencies which may not be immediately forseen, such as possible attack by oils and greases, ageing, attack by ozone or poor dynamic properties which reduce this choice considerably. Thus it is most important to define the requirements very carefully.

There are four essential stages in designing a rubber component for a given application.

These are:-

(a) Defining fully the requirement.
(b) Selecting the type of rubber to be used and designing or selecting a suitable compound at an economic cost.
(c) Designing the component.
(d) Defining the production method for the part.

2.1.1 The Requirement

The following headings need to be addressed:-

(1) The function of the component.
(2) The manner in which the component will be stressed i.e. in elongation, compression, vibration or torsion.
(3) Exposure to liquids, e.g. petroleum-based, hydraulic fluids, antifreeze or others.
(4) Expected life and storage conditions.
(5) Normal operating temperature, range over which the component must work effectively.
(6) Degredative conditions, e.g. atmospheric, sunlight, ozone abrasion.
(7) Electrical requirements.
(8) Flame resistance.
(9) Metals in contact during use.
(10) Any other requirement ie dynamic properties, special mechanical properties, colour ie non black.

2.2 Selection of Material

The physical properties of vulcanized rubber compounds can be varied over a wide range, dependent upon the type of rubber polymer used and the formulation of the compound. Variation of a compound to improve one property will usually affect other properties. For instance, an increase in hardness is usually accompanied by a decrease in resilience and elongation to break. Therefore compromise is necessary to obtain an optimum range of characteristics for the vulcanizate. Rubber specifications usually involve the reaching of a compromise between what is desired and what is practically achievable and expert advice should be sought early in the design study. Generally it is advantageous to carry out an initial trial under service conditions before finalizing the formulation. The physical properties which are considered to be of interest to engineers and designers are briefly outlined in the following clauses. These properties are also those that are usually encountered in rubber specifications.

2.3 Engineering Properties

2.3.1 Hardness

International Rubber Hardness Degrees. (IRHD) The hardness of a vulcanized rubber compound is related to the reversible elastic penetration produced by an indenter of specified dimensions under a given load (BS 903: Part A 26). It is quoted in International Rubber Hardness Degrees the scale being so chosen that zero represents a material of infinite softness (elastic modulus of zero) and 100 a material of infinite hardness (elastic modulus of infinity). A difference of one IRHD anywhere between 30 IRHD and 95 IRHD represents approximately the same proportionate difference in Young's modulus. Below 30 IRHD there is a marked deviation from the normal relationship to Young's modulus.

There is an approximate relationship between IRHD and the modulus of rubber compounds. (Table 1).

TABLE 1

HARDNESS AND ELASTIC MODULI

(Based on experiments on natural rubber spring vulcanizates containing, above 48 IRHD, SRF black as filler. Note that hardness is subject to an uncertainty of about ± 2 degrees).

Hardness IRHD ± 2	Young's Modulus E_o MN/m^2	Shear Modulus G MN/m^2	Bulk Modulus* E_{oo} MN/m^2
30	0.92	0.30	1000
35	1.18	0.37	1000
40	1.50	0.45	1000
45	1.80	0.54	1000
50	2.20	0.64	1030
55	3.25	0.81	1090
60	4.45	1.06	1150
65	5.85	1.37	1210
70	7.35	1.73	1270
75	9.40	2.22	1330

NOTE:- Theoretically, with a Poisson's ratio of 1/2, E_o should equal 3G. This is so for soft gum rubbers, but for harder rubbers containing a fair proportion of non-rubber constituents, thixotropic and other effects increase E_o to about 4G.

2.3.2 Shore Hardness. The Shore hardness scale is widely used in the USA and readings in IRHD are approximately the same as those of the Shore durometer type A over the range of 30 to 95 °. A direct conversion to IRHD is acceptable for all practical purposes.

2.3.3 Stress/Strain behaviour

Tension/compression.

The mechanism of rubber-like deformation makes it possible to predict by purely mathematical reasoning the shape of the stress/strain curve for rubber. This leads to the following expression for either simple elongation or compression.

$$f = G(\lambda - \lambda^{-2})$$

Where f = stress calculated on the original undeformed cross-section (the engineer must especially note that the rubber technologist's stress/strain curve always has the stress calculated in this way);

G = shear modulus;

λ = ratio of strained to unstrained length, the length being the dimension in the direction of deformation.

The form of this relationship between stress and strain is shown in Figure 1.

It must be noted that for the compression part of this curve it is assumed that the end surfaces of the rubber are not constrained by friction or bonding, so that for instance, a rectangular block on compression still retains a rectangular form.

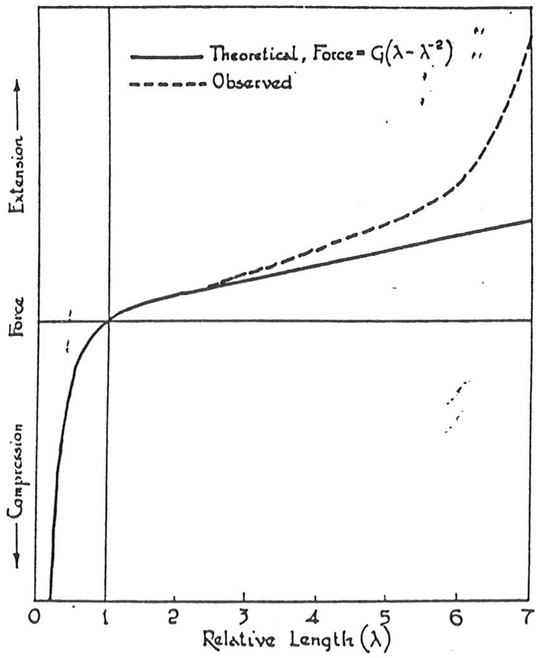


FIG. 1.1 Force versus relative length for rubber stressed in tension and compression

The important points shown by Figure 1 are that the stress is not directly proportional to strain and the tension and compression curves are continuous through the origin. Experiments confirm that deviations from the theoretical relationship occur at moderate elongations and these deviations become large at high elongations (dotted line) . The greatly increasing stiffness at high elongations is due mainly to the parallel alignment of the long rubber molecules; this can lead to crystallisation in some rubbers eg natural rubber and chloroprene.

The essential point to note is that the slope of the rubber stress/strain curve (ie tangent modulus) increases with increasing deformation, so that one cannot define the elastic behaviour of rubber simply by Young's modulus. Rubber technologists more commonly quote a "secant" modulus at a given elongation. Thus if a tensile stress of 10 MPa produces an elongation of 300% the compound is said to have a "300% modulus" of 10 MPa.

2.3.4 Shear

The stress-strain curves of rubbers in shear are substantially linear over the normal working strains (Figure 2). For soft rubber vulcanizates, the maximum design strain should rarely exceed 100% and is normally less than 50%. For hard vulcanizates, rather lower strains are used and the curves become less linear.

The shear modulus G is obtained from curves such as those in Figure 1.9 from

$$q = Ge_s$$

where the shear stress q is F/A (Force/Area) and the strain, e_s, is x/t (deflection/thickness). Approximate values of G for rubbers of different hardnesses are given in Table 1.

The shear stiffness K_s of a rubber mounting is

$$K_s = \frac{F}{x} = \frac{GA}{t}$$

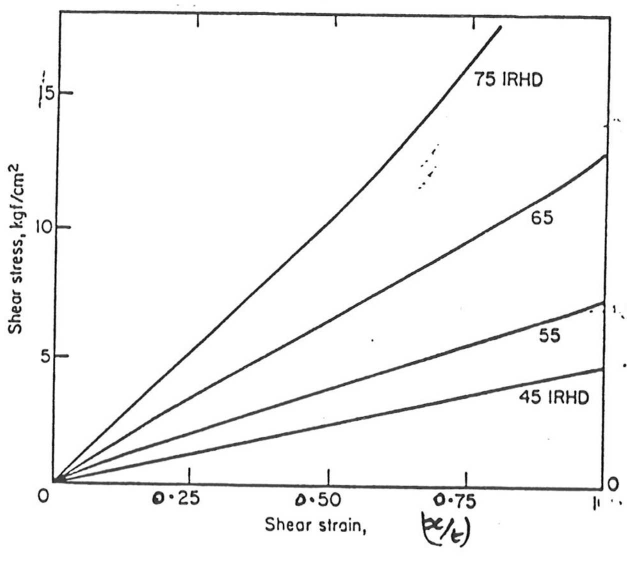


Figure 2. Typical shear stress/strain relationship for rubbers of different hardnesses.

2.3.5 Incompressibility

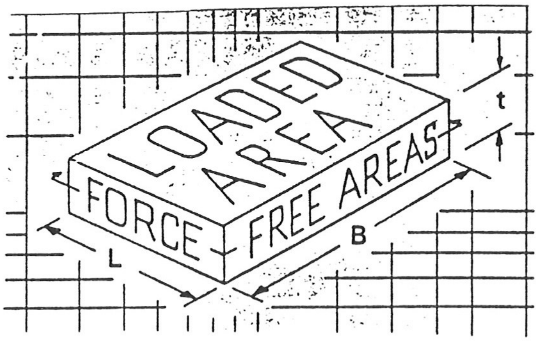
The bulk modulus of rubber Eoo (1000 - 2000 MN/m^2) is many times larger than its Young's modulus E_o and Poisson's ratio can be taken as 1/2. The very high bulk modulus means that rubber hardly changes in volume even under high loads, so that for most types of deformation there must be space into which the rubber can deform. The greater restriction on its freedom to deform the stiffer it will become, a feature used in the design of compression springs.

2.3.6 Shape Factor

Shape factor is a difficult point for many engineers. The fact that a block of rubber in compression may be made up to 30 times as stiff by the insertion of three metal plates to form a 3 layer sandwich is sometimes difficult to appreciate by one used to metals.

The stiffness of rubber in compression when the loaded surfaces are prevented from slipping (by bonding) depends on the shape factor.

Shape factor is defined for a rectangular block as the ratio of one loaded face area to the total unloaded area.



$$\text{shape factor} = \frac{\text{loaded area}}{\text{force free area}}$$

$$\text{i.e. } S = \frac{LB}{2t\,(L+B)}$$

The compression modulus depends on shape factor such that

$$E_c = E_o \ (1 + 2k \ S^2)$$

or where $S > 3$, $(E_c \sim 5GS^2)$

E_c = compression modulus
E_o = Young's modulus
S = shape factor
k = a numerical factor.

The compression stiffness is given by

$$K_c = \text{load/deflection} = \frac{E_c.A}{t} = \frac{5GAS^2}{t}$$

thus the stiffness can be seen to be very dependent on the shape factor.

2.3.7 Creep and stress-relaxation

Although the process of vulcanization leads to the elastic state becoming the more dominant characteristic in a rubber vulcanizate, it does not entirely eliminate all the viscous element of the rubber properties, so that when a constant stress is applied to the rubber the deformation is not constant but gradually increases with time; such increase is known as creep. Conversely when a rubber is subjected to a constant strain, a decrease in stress takes place; this behaviour is called stress relaxation. Both phenomena will be familiar to engineers; particularly with reference to the behaviour of metal springs and although the two effects are allied there is not a simple general relationship between them. At room temperature these effects are directly related to the viscous element and are comparatively small. But at high temperatures in addition to viscous flow, chemical processes occur such as oxidation which can result in either main chain or cross link scission and a subsequent change in the rate of creep and stress relaxation.

At temperatures well above ambient these chemical processes become of increasing importance and the extent to which they occur is dependent upon the nature of the polymer and upon the presence or absence of oxygen in the system. The effect of creep is of particular importance in the design of engineering components. Although the relative effects of variables upon creep have not been fully established, the following generalisations are of importance:

(a) Creep increases with increasing stress.
(b) Creep increases with increasing temperature.
(c) For equal stresses creep is greater under tensile stress than shear stress which has a greater effect than compressive stress.
(d) Creep is greater under dynamic loading than under static loading.
(e) Creep is dependent upon the nature of the polymer (hysteretic rubbers showing high creep) and upon state of cure, decreasing with increasing state of cure and increasing with high filler loadings.

2.3.8 Compression Set

Whan a rubber specimen is subjected to a distorting load, either in tension, compression or shear, it does not return to its original dimensions after release of the load, but exhibits a certain amount of deformation, the extent of the deformation being markedly dependent upon the amount and duration of the loading, upon the temperature at which the deformation is imposed and upon the time after release of load at which measurement is made. For most practical purposes it is the residual deformation after being subjected to a compression which is of greatest importance and this is termed compression set. It is defined as the residual contraction in a sample after it has been subjected to a compressive stress and then allowed to recover.

For test purposes, it may be measured under conditions of constant stress or of constant deflection (constant strain) but the latter is the test used in specifications since it approximates more closely to the majority of applications. Compression set can give a guide to the sealing behaviour of a rubber when used under compression, as in gaskets etc, although it may be only an indirect relationship. It should be realised that this test method measures the ability of a rubber to recover from a compressive stress but does not measure the behaviour of the rubber whilst under the compressive load (see creep and stress relaxation). Compression set is, however, one of the basic characteristics of a rubber compound since it is directly related to the extent of cross linking in the rubber and is therefore of great importance in controlling quality from batch to batch.

2.3.9 Dynamic properties of rubbers.

For many engineering purposes, rubber is subjected to oscillatory or impact stresses.

The most important environmental parameters which affect the dynamic modulus of a rubber are temperature, frequency and the amplitude of the imposed oscillation. Important compounding parameters are the degree and type of crosslinking and the amount and type of carbon black used to stiffen the compound.

The effects of temperature and frequency become prominent as the temperature decreases and approaches the glass transition of the rubber. The effects can be quite small at ambient temperatures. However the effects of amplitude can still be considerable at ambient. The modulus of a filled rubber under dynamic conditions can show a much higher value at low strains much below those at which measurements are normally carried out. Because many applications involving dynamic properties involve small strains this effect is important (Figure 3).

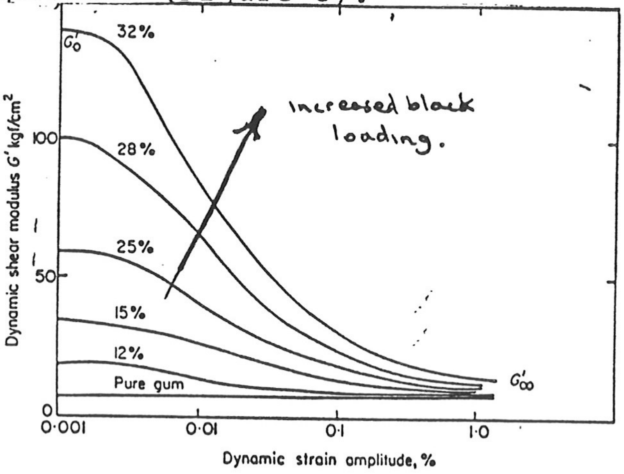


FIG. 3 Variation of shear modulus G' with strain amplitude of oscillation; natural rubber compound.

Hysteresis on the other hand is important at higher strains and is the work represented by the area between the loading and unloading curves in a load/deformation cycle. For some rubbers, ie butadiene and natural rubber there is little hysteresis up to moderate deformation. Other materials particularly some urethanes show high hysteresis. Figure 4 shows a typical set of hysterisis curves for natural rubber illustrating how hysteresis is high for the first few cycles only.

Rapidly repeated deformations can cause considerable hysteresis energy to be created which must be dissipated as heat. Rubbers are in general poor conductors of heat and the rise in temperature (heat build-up) may result in thermal degradation. Natural rubber, with its low hysteresis, is the preferred materials for dynamic vibration applications without the danger of serious heat build-up. Hysteresis is a measure of the energy lost; the converse is resilience, which is a measure of the energy returned. Both depend not only upon the type of polymer but also on the filler and other compounding ingredients.

The properties which are normally determined by the rubber technologist and published in manufacturers brochures are not appropriate to the design of components which are to be used under dynamic conditions. It is however, possible by experimental means to obtain sufficient data upon which a suitable design may be developed. In such cases the rubber specialists should be consulted at an early design stage, with details of the application, including applied load, frequency, amplitude etc.

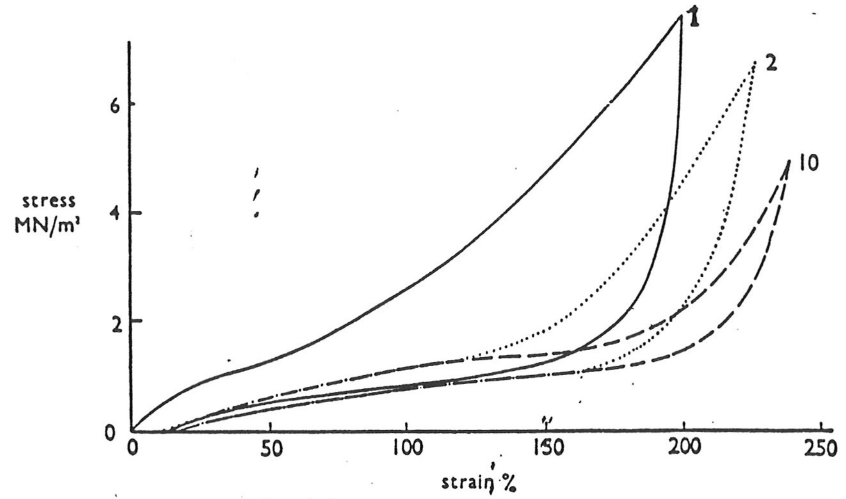


Fig. A—The first, second and tenth tensile stress-strain loops on a vulcanizate containing 50 parts reinforcing black. Most of the structure breakdown (and also set) occurs on the first cycle.

2.3.10 Swelling in liquids

When a rubber product is exposed to a liquid, provided that no chemical reaction occurs, two effects may be noticed. The more obvious is a change in dimensions due to swelling (which may be positive because of absorption of liquid, or negative because of extraction of soluble compounding ingredients eg ester plasticizers by fuels). Less apparent but sometimes of greater importance is the deterioration of physical properties. The significance of these effects may vary for the same compound and the same fluid, depending upon the applications and conditions of service.

All rubbers swell to some extent and no one rubber is suitable for operation in all fluids. It is necessary therefore to make a careful choice of the rubber to be used in any particular system. For many engineering applications the major interest to designers is the effect of mineral oil-based fuels and lubricants. Wherever possible, actual service trials should be carried out before a final decision is made of the rubber compound to be used.

The swelling of rubber by liquids is a diffusion controlled process and up to the equilibrium swelling ratio, the volume of liquid absorbed is proportional to the square root of the time for which the rubber has been immersed in the liquid.

For most organic liquids the rate of penetration also depends upon the viscosity of the swelling liquid rather than on its chemical nature. Thus the time to penetrate 5 mm is about four days for a mobile liquid like benzene, one to two years for an engine lubricating oil, and about thirty years for a thick grease such as Vaseline. As it is unusual for rubber mountings and springs to be used completely immersed in oil, adequate protection for many rubbers against oil splashes can normally be obtained by a suitable shield or by coating with an oil resistant paint. Occasional splashing is not serious, and the bulk of large components is generally a sufficient safeguard in itself.

2.3.11 High temperature use

In general, resistance to high temperature is a function of polymer structure, although some improvement can be made by compounding techniques which can change the order of the polymers listed under (a) to (g). As a general guide rubbers may be put in the following order of merit:

	UPPER TEMPERATURE FOR CONTINUOUS OPERATIONS (°C)
(a) Silicones, fluorosilicones and fluorocarbon rubbers.	250
(b) Ethylene-propylene rubbers, acrylate rubbers.	150
(c) Chloroprene rubber, chlorosulphonated polyethylene rubber, polysulphide rubbers, epichlorohydrins polypropylene oxide rubbers.	125
(d) Acrylonitrile-butadiene rubbers.	120
(e) Butyl rubbers.	110
(f) Styrene-Butadiene rubbers.	100
(g) Natural rubber.	90

2.3.12 Low temperature resistance

Behaviour at low temperatures is a function of polymer structure and mix formulation. As the temperature falls there is an increase in stiffness, the rubber passing through a leathery transition state to become a brittle solid. This change is characterized by time effects other than those required to attain thermal equilibrium and the ability of a rubber compound to function at low temperatures will depend not only on the chemical structure but also upon the size of the component and upon the rate and magnitude of the applied deformation. The use of a plasticizer may improve the low temperature behaviour, depending upon the efficiency of the plasticizer and upon the amount which may be tolerated, but the effectiveness of the plasticizer may be affected by the working conditions eg by contact with fuels etc.

For low temperature use rubbers may be put into the following groups. However it must be remembered that suitable compounding can change the low temperature limit by up to 20 °C.

(1) Good low temperature properties < - 55 °C.

Silicone, fluorosilicone, butadiene, isoprene and natural rubber,* propylene oxide rubbers.

(2) Moderate low temperature properties > - 55 < - 35 °C.

Butyl, ethylene propylene, SBR, polysulphide, polyetherurethanes, epichlorohydrins.

(3) Poor low temperature properties > - 35 °C.

Chloroprene,* nitrile, fluorocarbons, acrylates, chlorosulphonated polyethylene and polyester urethanes*.

* These rubbers may also show stiffening due to crystallisation if held at low temperatures for a long period. This phenomenon is usually reversible if the vulcanizate is held at a relatively high temperature for a period before use.

2.3.13 <u>Atmospheric attack (light ageing and ozone attack</u>

No rubber is completely stable with respect to age and it is known that many factors such as oxygen, ozone, sunlight, heat and mechanical conditions may markedly contribute to the deterioration of rubber with the passage of time.

Upon exposure to outdoor weathering, rubber vulcanizates are subject to a variety of conditions but the resulting effects (excluding the normal oxidative attack which proceeds concurrently) may be resolved into two distinct processes, the first being an oxidation process catalysed by light, normally known as light ageing, and the second, attack by ozone. Light ageing is a surface oxidative effect which occurs only on exposure to pale, particularly sunlight, and results in the formation of a hard resinous skin which upon exposure to rainfall or upon flexing of the rubber develops into an extremely random crazing. The effect of light ageing is more pronounced with unsaturated rubbers which are subject to oxidative attack and can be extremely rapid in light coloured articles. The effects, however, can be almost completely eliminated by the inclusion in the rubber formulation of carbon black. Rubbers of the silicone, fluorocarbon, ethylene-propylene and chlorosulphonated polyethylene types appear to be completely unaffected by light ageing and may therefore be used where coloured components are required.

Ozone concentration at the earth's surface has been shown to vary quite widely from about 0.5 to 10 parts per 100 milion not only geographically but also seasonally and even from day-to-day in any one particular locality. The conventional rubbers, such as natural rubber and butadiene-styrene rubbers can be markedly affected by ozone, with unprotected natural or butadiene-styrene rubber showing gross effects after a few days at 2.5 parts per 100 million or after a few hours at 25 parts per 100 million of ozone. Attack however can only occur if the rubber is subjected to tensile strain. Similar effects are obtained when these rubbers are exposed to a high concentration of oxides of nitrogen which may be present in the atmosphere particularly in industrial areas.

In addition to the effects which occur during the service life of a rubber component, it is obviously of importance to have information on the storage life. Recommendations for the storage of vulcanized rubbers are given in BS 3574.

2.3.14 Electrical Properties

All unfilled rubber vulcanizates may be regarded as normally having low conductivity, the non-polar (non-mineral oil resistant) rubbers being better than the oil resistant rubbers in this respect. Care must always be taken as these rubber vulcanizates may have a measurable, if low conductivity. The electrical properties however are markedly affected by the compounding ingredients used, particularly by the inclusion of such materials as carbon blacks and it is possible to formulate rubber compounds having volume resistivities between $10^{13}\,\Omega\mathrm{m}$ and $0.01\,\Omega\mathrm{m}$. Thus special compounding is necessary for both insulating and conducting vulcanizates. Because of the good insulation properties of most rubber vulcanizates, it is possible under certain conditions, for a large charge of static electricity to accumulate on a rubber component. Such conditions may be induced for instance, by the flow of air over an aircraft or vehicle, or by the flow of petrol through a fuel hose. By suitable compounding most rubbers may be made anti-static.

2.3.15 Compatibility with explosives

Although rubbers in general have no effect upon explosives many of the compounding ingredients in rubber vulcanizates tend to sensitize them. Where a rubber component is to be used in close proximity to an explosive (HE, propellant or initiator), guidance on the suitability or otherwise of the proposed rubber compound must be sought.

It is essential that care should be taken to ensure that only ingredients compatible with explosives are used in manufacture and a note to this effect must be included on drawings. In addition to the effect of the rubber on the explosive it is necessary also to consider the effect of the explosive on the rubber vulcanizate. It has been mentioned earlier that some rubbers are severely attacked by oxides of nitrogen. These may be present in certain types of ammunition and careful attention should be paid to design to minimize the amount of exposure of the rubber to these gases. Nitro-glycerine used in many propellants has a marked swelling effect on many rubbers. Where there is contact between such a propellant and a rubber component then use must be made of a compatible rubber. Such materials are designated QX rubbers.

2.3.16 Permeability to gases

For many applications the rate at which gases will pass through a rubber vulcanizate is of great importance, for instance in inner tubes, pneumatic shock absorbers and diaphragms. Rubbers differ considerably in permeability rate since this is affected by the size of the gas molecule and the solubility of the gas in the rubber. In general the silicone rubbers have the greatest permeability to gases followed by styrene-butadiene, natural, butadiene-acrylonitrile, polychloroprene, ethylene-propylene and butyl rubbers in decreasing order of permeability. Permeability increases rapidly with increasing temperature and decreases with increasing thickness of rubber.

2.3.17 Thermal expansion

All rubbers have a very high coefficient of thermal expansion compared with those of metals (about ten times that of steel) although this is affected by compounding, the more loaded (harder) rubbers vulcanizate having a lower coefficient than the soft rubbers. For most applications this difference is of little importance but it may become serious for applications at very low temperatures, for instance oil seals may shrink so that leakage occurs or rubber to metal bonded units develop undue stresses leading to premature failure.

2.4 Rubber Material Properties

The following section is intended to give a brief general description of the physical characteristics of individual types of rubber and should not be used as a design guide. The temperature range given for the operational use of the rubber is only intended as a general guide for long term service, and the user may have to establish with some initial trials the capability of the rubber to perform satisfactorily under his conditions. The abbreviations in brackets represents the agreed BS designation

2.4.1 Natural rubber and synthetic polyisoprene (NR and IR)

Natural rubber has high tensile strength over the full hardness range. Resistance to abrasion, heat, flex-cracking and cold flow is good and electrical properties and low temperature behaviour are excellent. The changes in physical properties over the range 0 to 70 ^{o}C are relatively small and it has the lowest hysteresis of all rubbers except polybutadiene. By special compounding techniques, natural rubber may be made suitable for use continuously at 90 ^{o}C and for short intermittent periods up to 120 ^{o}C. Incorporation of ester plasticizers into natural rubber makes compounds suitable for use down to - 80 ^{o}C although with such compounds the upper temperature limit may decrease. The resistance of natural rubber vulcanizates to mineral and petroleum based oils and fuels is poor although they are suitable in thick sections for intermittant contact ie engine mounts. Natural rubber is suitable with a wide range of inorganic and organic chemicals, such as castor oil based and polyglycol based hydraulic fluids. Natural rubber can be seriously affected by ozone, particularly under dynamic conditions, but the incorporation of certain waxes or antiozonants make it suitable for use under low strain static conditions. Resistance to sunlight and outdoor weathering is good for black compounds, but only fair for coloured or white compounds. Polyisoprene (synthetic natural rubber) although identical in chemical structure does differ in properties from natural rubber. It shows less tendency for crystallization to occur and is usually not used alone in compounds due to processing difficulties.

2.4.2 Styrene-butadiene rubbers (SBR)

These rubbers are the most widely used materials and are used extensively in general purpose applications where mineral oil resistance is not required and may be considered, except for dynamic applications, as a replacement for natural rubber.

Physical properties are in general slightly inferior to those of natural rubber but ageing characteristics are better and it may be used at somewhat higher temperatures. Low temperature behaviour is inferior to that of natural rubber but the rubbers show no tendency to crystallization. Vulcanizates have a useful operational range of - 45 to 100 °C. Polymers containing a high proportion of styrene are widely used in blends with natural rubber to give improved wear resistance and high hardness.

2.4.3 Isobutylene-isoprene rubbers-butyl (IIR)

The physical properties of butyl rubbers are generally poorer than those of natural and styrene-butadiene rubbers. Marked improvements may, however, be made by special compounding (resin curing), which also improves the heat resistance. The high hysteresis of butyl rubbers can be of use in applications requiring high damping characteristics. Ageing characteristics and electrical properties are very good and the butyl vulcanizates have excellent resistance to chemical attack (by ozone, acids, alkalis etc) and to weathering. They have the lowest permeability to gases of any rubbers and their biggest use is therefore in gas retention applications. Butyl rubbers are suitable for use in contact with many fluids, except for the mineral and petroleum based fluids, and may be used where resistance to phosphate ester hydraulic fluids is required. They are less affected by most explosives than other rubbers, although some difficulties with regard to compatability still remain. Operational range - 50 to 125 °C.

2.4.4 Ethylene-propylene rubbers (EPM), (EPDM)

Ethylene-propylene rubbers are available in two types - as the copolymer (EPM) which is cross-linked with peroxides or as a terpolymer (EPDM) which can be cross-linked with sulphur. The properties of vulcanizates prepared from the two types of polymer are very similar, the saturated copolymer (EPM) possibly showing slightly better retention of properties at higher temperature and on long term heat ageing. Both have excellent physical strength over the full hardness range and outstanding resistance to ozone, light ageing, oxidative and heat ageing and to many inorganic and organic chemicals (including phosphate ester hydraulic fluid) but resistance to mineral and petroleum based fluids is poor. Low temperature behaviour is good, approximating to that of butyl rubber and there are no effects due to crystallization on storage. Operational range - 50 to 150 °C.

2.4.5 Silicone rubbers (MQ)

Silicone rubbers are special-purpose rubbers developed mainly for high and low temperature applications. Physical properties are rather lower than for hydrocarbon rubbers, although grades having fairly good tensile and tear properties have recently been developed. The properties are less sensitive to temperature than all other rubbers over the operational range which is very wide.

Silicones have a tendency to creep and their resistance to petroleum based fluid is poor. Electrical properties are good and resistance to weathering and to ozone attack is outstanding. Under certain conditions, silicone rubbers may deteriorate, particularly if the design is such that the rubber is totally enclosed. In addition to the solid rubbers, silicone rubbers are also available as two part liquid or paste compounds which can be used as sealing or jointing compounds or for encapsulation of electronic equipment. These compounds vulcanize at room temperature in a few days, or in a few hours at elevated temperatures. A single shot (self-curing) grade is also available but care should be taken in the use of some of these materials in electronic equipment since they release acetic acid on curing. The operational range is dependent upon the grade, low temperature grades being usable over the range - 90 to 150 ^{o}C and high temperature grades over the range of - 45 to 250 ^{o}C. These rubbers are very expensive and should not be used for applications within the operational range of conventional rubbers (-50 to 120 ^{o}C) unless some special property of silicone rubbers, not obtainable by the use of other rubbers, is required.

2.4.6 Butadiene rubbers (BR)

Three types are produced, the high (97%) cis-1,4, polybutadiene the medium high (92%) cis 1:4 and the low (40%) cis-1,4, polybutadiene. This polymer is usually used in blends with other polymers, such as SBR where it improves abrasion resistance. This rubber, with the exception of silicone rubber, has the lowest glass transition temperature and the highest resilience of readily available rubbers.

2.4.7 Chloroprene rubbers (CR)

Chloroprene rubbers are classed as having medium resistance to petroleum based oils and fuels, with good physical properties over the hardness range 40 to 90 IRHD. Ageing and weathering resistance is excellent but care should be exercised with light coloured vulcanizate. Resistance to normal ground level ozone concentrations is good, whilst permeability to gases is fairly low. Although not fire resistant the inability of chloroprene rubbers to propagate flame or support combustion make them specially suitable for non-flammable applications. Electrical properties are poor and the rubber is not resistant to ester lubricants. In designs where contact with metal is involved, the possibility of corrosion must be considered. The behaviour at low temperatures is not very satisfactory but may be improved by the use of plasticizers. The operational range is - 40 to 120 ^{o}C.

2.4.8 Chlorosulphonated polyethylene (CSM)

Chlorosulphonated polyethylene is a low density polyethylene which has been chemically modified to enable vulcanization to be carried out. Vulcanizates have oil and fuel resistance approximately equivalent to the chloroprene rubbers with good physical properties over the hardness range 40 to 90 IRHD. Chemical resistance is very good, whilst permeability to gases is lower than that of the chloroprene rubbers. Resistance to weathering and ozone attack is extremely good especially in the case of coloured compounds. Ageing and heat resistance are better than the chloroprene rubbers and the behaviour at low temperature approximately in the same. Electrical properties are very good and the polymer is considered non-flammable. Operational range is - 40 to 150 °C.

2.4.9 Acrylonitrile-butadiene rubbers (NBR, Nitrile)

Nitrile rubber is the general purpose oil-resistant rubber. The oil resistance of nitrile rubbers is directly related to the acrylonitrile content, but low temperature resistance is inversely related to this so that the best oil-resistant grades have poor low temperature properties. The low temperature performance may be improved by the use of plasticizers.

Most specifications are based upon rubbers of intermediate (25 to 33%) acrylonitrile content and the oil and fuel resistance of such rubbers is superior to that of the polychloroprenes. Physical properties, heat resistance and low temperature resistance are roughly equivalent but weathering is poor and ozone resistance very poor. However, these latter properties may be improved by the addition of polyvinyl chloride. Blends of nitrile and PVC can be obtained from most manufacturers. To a lesser extent the addition of antiozonants also increases the resistance to weathering. Electrical properties are poor, although again compounds containing polyvinyl chloride show some improvement. However the inclusion of PVC does increase the possibility of corrosion of metal. The operational range is - 35 to 120 °C.

2.4.10 Fluorosilicone rubbers (FMQ)

Fluorosilicone rubbers are fluorine-modified silicone rubbers, designed to have a moderate oil and fuel resistance, equivalent to that of the chloroprene rubbers. They have marked resistance to diester lubricants but are not satisfactory for use with phosphate esters. Physical properties, as with other silicone rubbers, are poor but ozone and weathering resistance is excellent. The operational range for applications in contact with petroleum based fuels, hydraulic fluids and lubricants is - 65 to 150 °C, in contact with silicone and ester based fluids - 65 to 180 °C, and in air - 65 to 200 °C for continuous operation and up to 250 °C for intermittent periods. Like silicone these rubbers are very expensive and should be used only where their unique properties are necessary.

2.4.11 Fluorocarbon rubbers (FPM)

The fluorocarbon rubbers are special purpose rubbers designed to have marked resistance to heat, oil and chemical attack particularly against oxidizing fluids. They are however unsuitable for use with phosphate esters. Mechanical properties over the hardness range 60 to 90 IRHD are very good and are retained even after long term ageing at high temperatures. Resistance to weathering and to ozone attack is excellent but owing to the highly polar nature of these rubbers low temperature behaviour is very poor. Electrical properties are good and the rubbers are non-flammable. The cost of these rubbers is again high and should be considered in any design study. The operational range is - 20 to 250 ^{o}C, although for certain selected applications they may be considered for use down to - 40 ^{o}C.

2.4.12 Polyurethane rubbers

Polyurethane rubbers fall into two main chemical classes, polyester (AU) and polyether (EU), which differ in the nature of the polymer main chain. Both types of material are available as solid polymers and as two-part liquid systems and in addition to use as sealants the latter types may be used for the low pressure open casting of relatively complex shapes. Care is required with the two part systems since they contain isocyanates as curing agents.

Polyester urethanes

Polyester urethanes have resistance to petroleum-based fuels and oils between the chloroprene rubbers and the acrylonitrile butadiene rubbers but have extremely high tensile and tear strength, abrasion resistance and load bearing characteristics, over the hardness range 30 to 95 IRHD. However, their dynamic properties are generally poor. Resistance to oxidative attack and to ozone is very good but upon exposure to warm moist conditions, or to hot fluids containing moisture, the polyester urethanes can show rapid breakdown with marked loss in physical properties. These elastomers are therefore only considered suitable for long term use in temperate conditions.

Polyether urethanes

Polyether urethanes have resistance to petroleum-based fuels and oils inferior to that of the chloroprene rubbers. Resistance to hydrolytic degradation is markedly superior to that of polyesters, and the harder polyethers (80 IRHD) appear to be suitable for use under tropical conditions. Electrical properties are fairly good and these materials may be satisfactorily used in encapsulation. The operational range is - 30 to 100 ^{o}C but special compounds are available which are serviceable down to - 70 ^{o}C. Polyurethane (both polyester and polyether) are rated as self-extinguishing. Compression set and creep characteristics are generally only fair and all materials suffer high hysteresis loss and consequent heat build-up on flexing, so that these materials are best avoided in dynamic applications, except for low frequency use.

2.4.13 Polysulphide rubbers (TR)

Polysulphide rubbers are available in two forms, as solid rubbers for moulding, and as liquids for casting or sealant applications. Vulcanizates made from both solid rubber and casting grades have excellent resistance to petroleum based fluids and to oxidative and ozone attack. Resistance to fungal and bacterial attack is also excellent. Physical properties - tensile stength, compression set and abrasion resistance are comparatively poor, especially for those vulcanizates obtained from liquid polymers. Little use is made of the solid rubbers.

2.4.14 Polyacrylate rubbers (ANM, ACM)

These rubbers are usually copolymers of ethyl acrylate and a chlorine containing monomer such as 2-chlorethyl vinyl ether. Their vulcanizates have superior resistance to deterioration by hot hydraulic oil compared to nitrile rubber, as well as better heat resistance. Resistance to weathering and ozone is good, but resistance to water is relatively poor. Their minimum temperature of use is approximately - 20 °C but they are suitable for intermittent use in the temperature range 180 to 200 °C.

2.4.15 Epichlorohydrin rubbers (CO, ECO)

Two types are currently available, a copolymer of epichlorohydrin and ethylene oxide and a homopolymer. They have good chemical resistance, particularly to oil, water, acids and bases. They are resistant to ozone and are self-extinguishing. In applications involving contact with some metals corrosion can be a problem. They have a useful temperature range of - 40 to 125 °C.

2.4.16 Polypropylene oxide rubber (GPO)

This rubber has a low density and its resistance to weathering is good. It has a high resilience, excellent flex life and performs similarly to natural rubber. It has the advantage over natural rubber of good heat ageing, ozone resistance and moderate resistance to oils and fuels. This is a relatively new rubber and it is still being evaluated to establish its place in the spectrum of rubbers.

2.4.17 Cellular materials

Cellular rubbers consist of large numbers of small thin-walled cells filled with air or other gases. The cells may all be completely separated ie non-intercommunicating (closed-cell expanded rubber) or wholly or partially communicating (sponge rubber or latex foam open-cell) depending upon the method of manufacture. Cellular rubbers may be made from most of the rubbers mentioned and in general the properties are comparable with those of the solid but the bulk of industrial production is of polyurethanes. Care must be taken with many cellular products in contact with explosives and propellants since the residual blowing agent often makes the rubber incompatible. Advice should be sought at an early stage.

2.4.18 Thermoelastomes

A number of rubbery materials have been produced where the chemical structure is controlled in such a way that the molecule contains flexible and rigid blocks. Such materials include styrene/butadiene; urethanes, where the hard block is a short chain diol-isocyanate linkage and certain ethylene propylene compounds. These materials may be moulded as thermoplastics at high temperatures but on cooling the hard blocks aggregate, effectively forming psuedo-cross linking points for the flexible rubbery component.

Such materials are widely used in consumer durables such as cheap shoes, handbags etc. Their biggest disadvantage from an engineering view is limited temperature range and high creep rate.

3. FABRICATION

Only a brief outline is given here. Designers should consult expert sources for details of manufacture.

3.1 Compound Manufacture

Rubber compounds are produced using either powerful internal mixers and/or on horizontal two roll mills. Considerable heat is produced by the mixing process so machines must be water cooled to prevent prevulcanisation. Although many compounds are manufactured to in-house specifications there is a vast range of standard rubber formulations covered by British Standards and other international specifications. Whilst these latter mixes differ in specific detail they do have a common property requirement set in the appropriate standard.

3.2 Moulding

Moulding is the operation of shaping and vulcanising the plastic rubber compound, by means of heat and pressure. Fundamentally, all processes of moulding are similar, the ways of introducing the material into the mould distinguishing one technique from another. Because a chemical reaction takes place at high temperature, considerable shrinkage takes place after moulding. This is normally between 1.5 and 5% and may be variable in different directions in non-symetrical mouldings.

3.3 Fabrication Techniques

As noted earlier, raw rubbers require the addition of fillers and a suitable vulcanizing system to give a final rubber product. The shelf life of an unvulcanised rubber compound is normally relatively short, so unlike the plastics industry, where specified materials are supplied ready compounded in bags, within the rubber industry the compounder is usually the manufacturer of the final component.

The main processes are compression moulding (the oldest and still most universally used process), transfer moulding and injection moulding.

3.3.1 Compression moulding

Compression moulding is essentially the squeezing of a blank of rubber, which may or may not be preheated, into a cavity form in a hot mould tool held between two heated press platens. The mould is held closed under pressure until the rubber component is cured, at which time it can be removed from the mould without damage and another blank inserted.

Many types of component are produced by this method with little difficulty, but, unless careful mould design is undertaken some components present too difficult a form to fill by compression flow.

3.3.2 Transfer Moulding

Transfer moulding is a more suitable process for parts of lower flash, difficult form, or where rubber to metal bonds are to be made. The mould cavity is similar to that for a compression mould but the rubber is placed in a subsidiary chamber usually cut into the top plate of the mould and subsequently forced through an orifice into the cavity by an integral ram when the press is closed.

The energy necessary to force the rubber from the transfer chamber into the cavity increases the temperature of the rubber compound considerably thus significantly reducing the cure times and the high pressure ensures the cavity is totally filled.

3.3.3 Injection Moulding

Injection moulding of rubber is similar to that of thermoplastics except that the injection barrel is run relatively cool so that the rubber does not set up whilst the mould is oil heated to give an ultra-rapid cure. This process is also very suitable for metal bonded parts.

Special machines have been developed to deal with one and two component liquid silicone rubber compounds.

Rubber injection moulding is only considered where numbers off are very high and is not yet suitable for all compounds and part shapes.

3.3.4 Extrusions

Rubbers can readily be extruded to form complex sections. However the profile still has to be cured. There are a number of accepted ways of effecting a good cure including fluidised beds, air tunnels and high pressure steam. The main problems are the retention of profile accuracy and elimination of porosity.

3.3.5 Calendering

Rubber is also calendered into flat sheet for instance for conveyor belts. A calender is effectively an array of heated metal rollers through which a rubber compound is passed, so that it is consistently fed and gauged to produce a uniform continuous sheet. The sheet may be laminated with a textile reinforcement as necessary.

4. STANDARDS

4.1.1 Component Design

In contrast, to many plastics applications where the sole reason for use is metal replacement, low weight, or reduction in cost. Rubbers are used in applications where their unique properties are called upon. This means that for the major application areas of rubbers e.g. tyres, seals, springs and mountings, the design considerations are well documented in standard texts. There is also more design freedom since cured rubber is elastic and therefore it is to possible accommodate undercuts and cores without expensive tooling.

However, when rubber is hot it is very weak; hence very thin sections are difficult to remove from moulds and because of mould shrinkage high tolerances are difficult to achieve. Suggested tolerances for commercially moulded components are given in BS3734. The main problems in design are those associated with metal bonded items such as springs. Rubber should not normally be used in springs in tension. Where it is, it is most important to avoid zero strain. A significant improvement in fatigue life is shown if zero strain is avoided. (Figure 5).

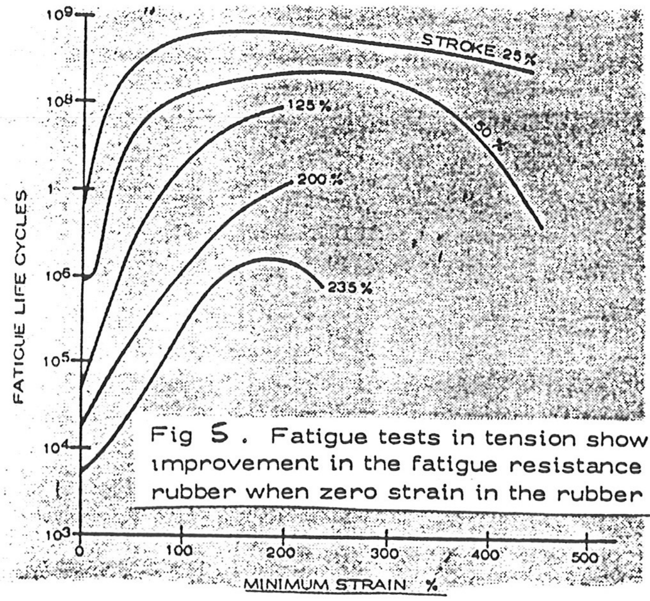


Fig 5. Fatigue tests in tension show a large improvement in the fatigue resistance of natural rubber when zero strain in the rubber is avoided.

The avoidance of sharp corners and stress concentrations near the bond is also of major importance thus radii should be as generous as possible. (Figure 6).

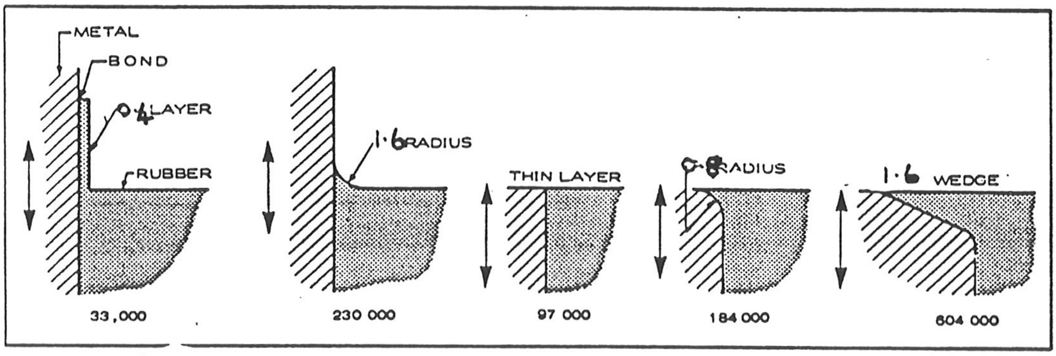


Fig. 6. Effect of reducing stress concentrations on the fatigue life of 25 square × 3·2 mm thick test pieces of natural rubber subjected to cyclic shear deformations of ± 100 per cent strain at 130 cycles per minute. Large flaws visible at the number of cycles shown.

For new or novel applications it is essential that a rubber materials specialist is consulted at the earliest possible design stage to avoid expensive mistakes occuring.

4.2 Quality Assurance Tests

Apart from normal dimensional checks and visual examination to confirm freedom from imperfections, such as blisters, weld lines and contamination in mouldings, it is normal practice in the rubber industry to mould a test sheet from the batch of material in use and undertake the following tests.

4.2.1 Density

Measurement of the density and comparison with the nominal value provides some assurance of the correct and consistent composition of the compound.

4.2.2 Chemical Requirements

These tests confirm that the concentration of impurities such as phenols, formaldehyde, lead and ammonium compounds, chloride and sulphate, which may sensitise explosives, or promote the corrosion of nearby metallic components, are kept to acceptably low levels. These tests would always be carried out for materials in close contact with explosives and propellant.

4.2.3 Hardness

This is a useful quality control test. See Section 2.3.1.

4.2.4 Tensile Properties

The tensile strength and elongation at break are normally used as Quality Control tests and appear in all specifications. In addition the value of the tensile stress at 100% elongation, 200% elongation, which are termed the 100% modulus, 200% modulus, etc. are also quoted.

4.2.5 Ageing

It is common practice to age samples cut from the test sheet for a specified period, 7 days at 100 ^{o}C for example, and then retest the samples. This gives some indication of the ageing behaviour of the compound and checks that even if the initial properties are correct, a suitable antidegredant system has been added to the formulation.

4.2.6 Swelling

Those rubbers which have a requirement to resist swelling in particular environments, for instance, oil seals, will also have a swelling requirement in the Quality Assurance tests.

A range of standard ASTM oils is available to be used for standard tests.

4.3 Responsibility of the Designer

In addition to the normal engineering requirements such as dimensional tolerances, the designer will need to define the quality required by stating special requirements on the drawing.

These requirements include:-

(a) The specification and the colour of the rubber compound and where necessary, the manufacturing process to be used eg compression, transfer or injection moulding.

(b) Any limitations on mould design, such as position of gate, flash, or pin marks which could affect the properties, assembly, or operation of the component.

(c) Details of inserts, if any.

(d) The positions, dimensions, and details of identification marks.

(e) Post-moulding treatments, such as post-curing.

(f) The maximum size and location of any minor defects which are acceptable.

(g) Any requirement for mechanical tests on the component, or on samples cut from the component.

(h) Special requirements such as resistance to fire, electrical tests, special tests for filled materials or compatibility requirements.

(i) Any special storage and packageing requirements.

4.4 Responsibility of the Manufacturer

Since the physical and mechanical properties of mouldings can be adversely affected by incorrect mould design and incorrect moulding conditions, it is essential that manufacture is carefully controlled. It may be necessary for the Design Authority to approve a mould design for critical parts. Before allowing bulk manufacture a contractor should be required to establish moulding procedures acceptable to the Quality Assurance Authority. After first-off mouldings have been declared acceptable, the moulding procedure shall be controlled and records of all procedures and machine settings must be retained during bulk manufacture.

5. REFERENCES

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2.	Use of Rubber in Engineering	Ed. P W Allen, P B Lindlay and A R Payne McLaren London 1967
3.	Engineering Design with Rubber	A R Payne and J R Scott McLaren London 1960
4.	Seal Users handbook	R M Austin and B S Nace BHRA Cratfield England
5.	Rubber Technology and Manufacture	C M Blow Butterworths 1971
6.	Physical Testing of Rubber	R P Brown Applied Science 1979

ANNEX A

LIST OF SPECIFICATIONS, ARRANGED IN NUMERICAL ORDER

1. In specifications for rubber components, the tests employed are chosen for their reproducibility and ability to control the properties of the material used; they are not normally intended to be simulated service tests. For Government Department applications guidance should be sought from the appropriate authority on the correct specification to be used in any application. Where a rubber compound has to be specially designed for an application and so does not fall within the scope of an existing specification, arrangements should be made with RO Waltham Abbey, for a specification to be prepared to cover the requirement.

2. BRITISH STANDARDS

BS 903	Methods of testing vulcanized rubber.
BS 1154	Vulcanized natural rubber.
BS 115	Vulcanized natural rubber for extrusion.
BS 1672	Methods of testing natural rubber latices.
BS 1673	Methods for testing raw rubber and unvulcanized compounded rubbers.
BS 1674	Specification for equipment and general procedure for mixing and vulcanizing rubber test mixes.
BS 1806	Tolerances and dimensions of toroidal sealing rings (imperial).
BS 2044	Laboratory tests for resistivity of conductive and antistatic rubbers.
BS 2050	Electrical resistance of conductive and antistatic products made from flexible polymeric material.
BS 2751 & 3222	Vulcanized butadiene-acrylonitrile rubbers.
BS 2752	Vulcanized chloroprene rubbers.
BS 3227	Vulcanized isobutylene-isoprene (butyl) rubbers.
BS 3397	Testing synthetic rubber latices.
BS 3558	Glossary of terms used in the rubber industry.
BS 3574	Recommendations for storage of vulcanized rubber.

BS 3734	Schedule of tolerances for rubber products in solid rubber and ebonite.
BS 4398	Compounding ingredients for rubber test mixes.
BS 4443	Methods of test for flexible cellular materials.
BS 4518	Tolerances and dimensions of toroidal sealing rings (metric).
BS 5176	Classifications system for vulcanized rubbers.
BS 5324	Guide to application of statistics to rubber testing.
BS 6014	Ethylene propylene rubber compounds.
Aero F68	Vulcanized rubber aircraft materials and components, storage.
Aero F69	Vulcanized rubber aircraft materials and components, packing and identification.

3. DEFENCE STANDARDS

DEF STAN 93-3/1	Vulcanized chloroprene rubber, type QX. Superceded.
DEF STAN 93-4/1	Vulcanized butyl rubber, type X.
DEF STAN 43-21/2	Chloroprene rubber cellular minimum tarnishing.
DEF STAN 93-31/1	Requirements for the quality assurance of fully compounded unvulcanized rubber.
DEF STAN 93-22/1	Butyl rubber black type MD.
DEF STAN 93-25/1	Chloroprene rubber black type MD.
DEF STAN 93-30/1	Natural rubber compounds type QX.
DEF STAN 93-31/2	Test procedures and process requirements for fully compounded unvulcanised rubber.
DEF STAN 93-44/1	Natural and synthetic isoprene rubber compounds.

4. MOAD SPECIFICATIONS

TS 370	Compounded, butadiene/acrylonitrile, antistatic, hardness 84-88 °.
K 409	India rubber, vulcanized.
TS 10087	Natural rubber, type MD (compounds 1-9).
TS 350	Butyl rubber compound 90 ° BS.
TS 10013	Butyl rubber non-dermatitic hardness 40 ° black.
TS 10014	Chloroprene rubber non-dermatitic, hardness 45 ° black.
TS 10043	Fluorocarbon rubbers type QX.
TS 10057	Natural rubber black type QX electronically conducting hardness 60 °.
TS 279	Natural rubber low temperature type.
TS 10054	Natural rubber red, Type QX.
CS 3105	Natural rubber for use with explosives.

5. DTD SPECIFICATIONS

DTD 458A	Rubber parts for use with mineral base hydraulic fluid.
DTD 552	Rubber parts for use with engine lubricating oil.
DTD 560	Rubber parts for use with aviation fuel.
DTD 565	Rubber parts for use with ethylene glycol.
DTD 784	Rubber materials for fuel hose.
DTD 818	Silicone rubber.
DTD 867	Cellular vulcanized rubber for self sealing fuel tanks (fighter type).
DTD 5508	Rubber for face piece mouldings of oxygen masks types 'H' and 'J'.
DTD 5509	Synthetic rubber resistant to engine lubricating oils, greases and fuels.
DTD 5514A	Vulcanized polychloroprene rubbers for aircraft.
DTD 5531	Vulcanized general purpose silicone rubbers for aircraft.

DTD 5543A	Vulcanized fluorocarbon rubbers for aircraft.
DTD 5582	Oil resistant vulcanized silicone rubbers for aircraft.
DTD 5583	Vulcanized fluorosilicone rubbers for aircraft.
DTD 5594	Vulcanized butadiene-acrylonitrile rubbers (mineral oil resistant) for aircraft.
DTD 5595	Vulcanized butadiene-acrylonitrile rubbers (fuel and synthetic oil resistant) for aircraft.
DTD 5596	Vulcanized ethylene-propylene rubbers (general purpose) for aircraft.
DTD 5597	Vulcanized ethylene-propylene rubbers (fluid resistant) for aircraft.
DTD 5612	Vulcanized fluorocarbon rubber (low compression set) for aircraft.
DTD 5614	Silicone rubber, facepieces for oxygen masks.
DTD 5615	Vulcanized silicone rubbers (high tear strength) for aircraft.

6. RO SPECIFICATIONS

RO 10530-01	Ethylene propylene rubber type QX.
RO 10562-01	Ethylene propylene rubber for thermal insulation.
RO 10637-01	Silicone rubber type QX.
RO 10640-01	Expanded silicone rubber type QX.
RO 10003-01	Ethylene propylene rubber type QX sheet grade 7225.

ROYAL ORDNANCE

Defence systems, sub-systems and components