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## Chapter 27: Polymers: Types, Properties and Applications

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#### Chapter 27

### Polymers Types, properties and applications

#### 27.1 Polymeric materials

Polymers are produced by combining a large number of small molecular units (monomers) by the chemical process known as polymerisation to form long-chain molecules. There are two main types. Thermoplastics consist of a series of long-chain polymerised molecules. All the chains of the molecules are separate and can slide over one another. In thermosetting polymers the chains become cross-linked so that a solid material is produced which cannot be softened and which will not flow.

Polymers are usually made in one of two polymerisation processes. In condensation-polymerisation the linking of molecules creates by-products, usually water, nitrogen or hydrogen gas. In addition-polymerisation no by-products are created. Both thermosetting and thermoplastic polymers can be manufactured by these processes.

#### 27.1.1 Thermoplastic polymers

The long-chain molecules of a thermoplastic polymer are held together by relatively weak van der Waals forces (Chapter 1), but the chemical bond along the chain is extremely strong (Figure 27.1. (a)) When the material is heated, the intermolecular forces are weakened and the polymer becomes soft and flexible; at high temperatures it becomes a viscous melt. When it is allowed to cool again it solidifies. The cycle of softening by heating and hardening by cooling can be repeated almost indefinitely, but with each cycle the material tends to become more brittle.

Thermoplastic materials can have either a semi-crystalline ordered structure or an amorphous random structure. Civil engineering materials such as Polypropylene, Nylon 66 and polycarbonate are examples of amorphous thermoplastic polymers. Developments in the field of engineering polymers include the introduction of high-performance polymers, such as polyethersulphone (PES), which is amorphous, and polyetheretherketone (PEEK), which is semicrystalline; these polymers offer properties far superior to those of the normal thermoplastic polymers. They are not normally employed in civil engineering due to their high costs but they are used in the aerospace engineering (Hollaway and Thorne, 1990).

#### Figure 27.1 here

#### 27.1.2 Thermosetting polymers

The principal thermosetting polymers which are used in construction are polyesters, vinylesters and epoxies. They may be used for two different functions, firstly they are combined with a fibrous material to form a composite or secondly as an adhesive; in the latter case the epoxies are generally used (see section 27.4.2). Thermosetting polymers are formed in a two-stage chemical reaction

when a polymer (e.g. polyesters, vinylesters and epoxies) is reacted with a curing agent, (e.g. Triethylene-tetramine [TETA]). Firstly, a substance consisting of a series of long-chain polymerised molecules, similar to those in thermoplastics, is produced; then the chains become cross-linked. This reaction can take place either at room temperature or under the application of heat and pressure. As the cross-linking is by strong chemical bonds, thermosetting polymers are rigid materials and their mechanical properties are affected by heat.

There are two basic procedures which are used to polymerise the thermosetting polymers for use in the civil engineering industry; these are the cold cure systems that are cured at ambient temperatures and the hot cure polymers where the polymerisation is performed at elevated temperatures. Thus different resin and curing systems are required for site and factory manufacture of fibre-reinforced polymer (FRP) composites, (e.g. the cold cure systems for site work and the hot cure systems for factory fabrication). Consideration must be given to the glass transition temperature, (Tg), of cold cure epoxy polymers.

#### 27.1.3 Foamed polymers

A rigid foam is a two-phase system of gas dispersed in solid polymer, and is produced by adding a blowing agent to molten resin. In the exothermic polymerization reaction the gas is released and causes the polymer to expand, increasing its original volume many times by the formation of small gas cells. Like solid polymers, rigid foam polymers can be either thermoplastic or thermosetting and generally any polymer can be foamed.

#### 27.2 Processing of thermoplastic polymers

Thermoplastic polymers may readily be processed into sheets or rods or complex shapes in one operation, which is often automated. Stages such as heating, shaping and cooling will ideally be a single event or a repeated cycle. The principal processing methods are extrusion, injection moulding, thermoforming and calendering.

The first is the most important method from the civil engineering viewpoint, and this is therefore outlined below. Powder or granules of thermoplastic polymer are fed from a hopper to a rotating screw inside a heated barrel; the screw depth is reduced along the barrel so that the material is compacted. At the end of the barrel the melt passes through a die to produce the desired finished article. Changing the die allows a wide range of products to be made, such as:

- profile products;
- film-blown plastic sheet;
- blow-moulded hollow plastic articles;
- co-extruded items;
- highly orientated grid sheets.

#### 27.2.1 Profile production

With different extrusion dies, many profiles can be manufactured, such as edging strips, pipes, window-frames, etc. However, success depends upon the correct design of the die.

#### 27.2.2 Film-blown plastic sheet

Molten plastic from the extruder passes through an annular die to form a thin tube; a supply of air inside the tube prevents collapse and when the film is cooled it passes through collapsing guides and nip rolls and is stored on drums. Biaxial orientation of the molecules of the polymer can be achieved by varying the air pressure in the polymer tube, which in turn controls the circumferential orientation. Longitudinal orientation can be achieved by varying the relative speeds of the nip roll and the linear velocity of the bubble; this is known as draw-down.

#### 27.2.3 Blow-moulded hollow plastic articles

A molten polymer tube, the Parison, is extruded through an annular die. A mould closes round the Parison and internal pressure forces the polymer against the sides of the mould. This method is used to form such articles as bottles and cold water storage tanks. The materials commonly used are polypropylene (PP), polyethylene (PE) and Polyethylene Terephthalate (PET).

#### 27.2.4 Co-extrusion items

A multilayered plastic composite is sometimes needed to withstand the end use requirements. Two or more polymers are combined in a single process by film blowing with an adhesive film between them. Reactive bonding processes to chemically cross-link the polymers are under development.

#### 27.2.5 Highly orientated grid sheets

Polymer grids are used in civil engineering as the reinforcement to soil in reinforced earth. Continuous sheets of thermoplastic polymers, generally polypropylene or polyethylene, are extruded to very fine tolerances and with a controlled structure. A pattern of holes is stamped out in the sheet and the stampings are saved for re-use. The perforated sheet is stretched in the longitudinal and then in the transverse direction to give a highly orientated polymer in the two directions with a tensile strength similar to that of mild steel. The low original stiffness of the material can be increased ten-fold. The elastic modulus of unorientated high-density polyethylene (HDPE), for instance, is initially only 1 GPa and after forming into an orientated molecular structure it increases to 10 GPa. The use of these sheets is discussed later in this chapter.

In injection moulding, softened thermoplastic polymer is forced through a nozzle into a clamped cold mould. When the plastic becomes cold, the mould is opened and the article is ejected; the operation is then repeated.

#### 27.3 Polymer properties

#### 27.3.1 Mechanical Properties

Thermoplastic polymers which are not cross-linked derive their strength and stiffness from the properties of the monomer units and the high molecular weight. Consequently, in crystalline thermoplastic polymers there is a high degree of molecular order and alignment, and during any

heating the crystalline phase will tend to melt and to form an amorphous viscous liquid. In amorphous thermoplastic polymers, there is a high degree of molecular entanglement so that they act like a cross-linked material. On heating, the molecules become disentangled and the polymer changes from a rigid solid to a viscous liquid.

The thermosetting polymers used in construction are reinforced with glass, aramid or carbon fibres to form the fibre/matrix composite for civil/structural utilisations. These polymers are cross-linked and form a tightly bound three dimensional network of polymer chains; the mechanical properties are highly dependent upon the network of molecular units and upon the lengths of cross-link chains. The characteristics of the network units are a function of the polymers used, their curing agents and the heat applied at the polymerisation stage. In addition, the length of the cross-linked chains is determined by the curing process. The most satisfactory way to cure polymers (and hence composites) is by the application of heat thus achieving optimum cross-linking and hence to enable the mechanical properties to realise their potential. Shrinkage of the polymer during curing does occur, particularly with polyesters; thus contraction on cooling at ambient temperature can lead to stress build-up between the matrix and fibre of a composite. This effect is caused by the differences between the thermal expansion coefficients of the matrix and fibre, and it can have a major effect on the internal micro-stresses which are sometimes sufficient to produce micro-packing, even in the absence of external loads; this will be discussed later. Table 27.1 gives the most important mechanical properties of the common thermosetting and thermoplastic polymers used in civil engineering.

#### Table 27.1 here

#### 27.3.2 Time-dependent characteristics

The deformation of a polymer material over time under the application of a constant load is referred to as the creep of that material; this deformation will continue as long as the load is applied. Upon removing the load the polymer will regain some of its original length but will not return completely to its original condition. Figure 27.2 illustrates the total creep curve for a polymer under a given uniaxial tensile stress at constant temperature; it is divided into five regions, similar to those described in Chapter 2. The reason for this characteristic is that a polymer has both the properties of an elastic solid and a viscous fluid. Consequently, polymer materials have mechanical characteristics which lie somewhere between the ideal Hookean materials, where stress is proportional to strain, and the Newtonian fluids, where stress is proportional to rate of strain. Thus they are classified as a visco-elastic material and their stress ( $\sigma$ ) is a function of strain ( $\epsilon$ ) and time (t), as described by the equation:

$$\sigma = f(\varepsilon, t) \tag{27.1}$$

#### Figure 27.2 here

This non-linear viscoelastic behaviour can be simplified for design purposes:

 $\sigma = \varepsilon f(t) \tag{27.2}$ 

This linear viscoelastic response indicates that, under sustained tensile stress, after a particular time interval the stress is directly proportional to strain. Figure 27.3 describes the various types of response discussed above for tensile testing stress–strain curves.

#### Figure 27.3 here

The creep, flow and plastic deformation in the polymeric materials results from the irreversible slippage, decoupling and disentanglements of the polymer chains in semi-crystalline polymers. An important consequence of the time-dependent behaviour of polymers is the stress relaxation when they are subjected to a particular constant strain; the stress necessary to maintain this strain decreases with time.

The creep of the polymeric material depends upon

- (i) The time-dependent nature of the micro-damage in the composite material subjected to stress.
- (ii) molecular characteristics and microstructure
- (iii) The loading histories and, the nature of the applied load.
- (iv) The temperature and moisture environments into which it is placed.

In assessing the creep of a polymer material it is particularly important to ensure that the service temperature does not approach the glass transition temperature of the polymer. As the polymer approaches this temperature its mechanical characteristics change.

Figure 27.4 illustrates a family of creep curves (Figure 27.2b) used to construct an isostrain curve of stress –Log time (Figure 27.4a), and a family of isochronous stress–strain curves including a 100s one (Figure 27.2c). The first and third curves have been produced by cross-plotting, from the family of creep curves at constant times. Constant load tests are carried out under controlled conditions, as required by BS 4618-5.3: (1972), at durations of 60s, 100s, 1h, 2h 100h, 1 year, 10 years and 80 years and the 100s isochronous stress–strain curve is a plot of the total strain (at the end of 100s) against the corresponding stress level as shown in Figure 27.4c. The three dimensional creep graph shows the relationships of curves (a), (b) and (c) on one graph. The creep modulus of the material may then be found by measuring the slope at any specific stress level on the isochronous stress–strain curve; the creep modulus will vary for every stress level.

Isostrain stress–Log time and isochronous stress–strain curves are generally different from stress relaxation–Log time and tensile testing stress–strain curves, respectively. This is owing to the different testing conditions as a creep test (constant stress) is different to a stress relaxation test (constant strain). However, it is usually experimentally easier to keep the stress constant and thus due to practical considerations, creep data are often used in design as adequate approximations in the way described above and shown in Figure 27.4.

#### Figure 27.4 here

Aklonis and MacKnight (1983) developed the time temperature superposition principle (TTSP). It is based upon the observation that the short term behaviour of viscoelastic materials at higher temperatures is similar to the long-term behaviour at some lower reference temperature (Cardon et al, 2000). The TTSP assumes that the effect of increasing temperature is equal to expanding the time of the creel response by a shift factor, such that creep curves made at different temperatures are superimposed by horizontal shifts along a logarithmic time scale to give a single curve that describes the creep response over a larger range of time or the master curve (ASTM D2990, 2001; Goertzen and Kessler, 2006). Thus the TTSP allows for short-term creep curves at a range of temperatures to be used to generate a creep compliance master curve that is much longer than the short-term creep curve. The method can be used for polymers and polymer composites

When applied to the generation of a creep master curve the following steps are required.

- A master specimen is subjected to a constant load at a certain temperature as in conventional creep tests.
- Similar experiments are performed for identical specimens at different temperature levels and the relevant creep curves drawn.
- An arbitrary reference temperature is selected
- All the individual creep curves corresponding to different temperature levels are shifted along the (*log* time) co-ordinate to obtain the superimposed master curve.

The shift process is shown diagrammatically in figure 27.5

#### Figure 27.5 Here

Cheng and Yang (2005) developed the (TTSP) further by introducing a matched theoretical calculated curve from a supposed model of transition kinetics in which only time is involved as the independent variable. Cessna (1971) developed the time, applied stress superposition principle (TSSP)), this principle can also estimate creep values for polymers and polymer composite materials.

#### 27.4 Applications and Uses of Polymers

#### 27.4.1 Sealants

Sealants are elastomeric materials which can be used for sealing joints against wind and water in construction. Thin curtain wall construction employs highly effective materials to provide the heat installation, but generally there is no cavity for the dispersion of water that may leak through the joints on the outside. In addition, in the event of air blowing directly to the inside of a joint there must be an effective material to provide heat insulation, consequently, a baffling system to provide this must be installed. Therefore, adhesive and elastic sealants are required to enable this type of construction to be used efficiently.

The largest variety of sealants fall into the classification of solvent release and are composed of three component parts:

- (a) the basic non-volatile vehicle (the liquid portion of the compound),
- (b) the pigment component,

(c) a solvent or thinner to make application easier.

The non-volatile vehicle can vary from a vegetable oil (eg. linseed) to a synthetic elastomer. Opacity or colour will be introduced into the material by the pigment component. To enable the sealant to be applied easily and to ensure the correct thickness is achieved a solvent is introduced. The sealant is cured and its required viscosity is reached by the evaporation of the solvent. The butyl rubber solution and the acrylic copolymer solution fall into this category.

Another group of sealants are those which are chemically cured. The polysulphide compounds and the silicone based compounds are the main sealants under this heading. The latter, which is a two part sealant, is highly dependent upon the environmental conditions for its rate of cure, thus, if the temperature and humidity are low, the curing period could be very long. The chemically cured compounds require adhesion additives in order to develop bond to a surface as they do not generally contain much solvent.

The desired properties of a sealant are:

- a good adhesion with the joint
- low rate of hardening
- low rate of shrinkage
- permanent elasticity.

The choice of sealants is a compromise as no one product has all the above mentioned attributes.

#### 27.4.2 Adhesives

Within the context of the construction industry the term adhesive embraces not only those materials which are used to bond together two components of a structure, but also those materials which provide a specific function in themselves (e.g. protection, decoration) and are at the same time self-adhesive to the substrate whose surface they modify. Thus, a mortar which may be used to bond bricks together may also be applied as a self adhesive protection and often decorative rendering over the finished block work.

In this section adhesive bonded connections are the primary concern. The physical nature of the fibre/matrix composites does introduce problems that are not encountered in metals. The fibre type and arrangement, as well as the resin type and fibre volume fraction will influence the behaviour of the joint. In addition, composites are not generally homogeneous throughout their thickness as many thermosetting polymers have gel coats applied to the laminating resin to protect it against aggressive environmental influences met with in construction; the resin rich surface layers will thus be brittle and when overloaded, are liable to display a brittle fracture. An appropriate resin should therefore be chosen, such as a compliant one, which will distribute the applied load over a large area, thus reducing the stress taken by the friable surface of the composite. There are two particular problems associated with adhesive bonding of FRP materials:

- the attachment to the surface of a layered material
- the surface may be contaminated with mould release agents remaining on it from the manufacturing procedures.

As the matrix material in a polymer composite is also an organic adhesive, the polymers which are then used to join composite materials together are likely to be similar in terms of chemical composition and mechanical properties. Currently the epoxy and the acrylic based toughened adhesives are used for general application and have proved over the years to be very versatile and easy to use, they are durable, robust and relatively free from toxic hazards; the toughened adhesives exhibit high pull strengths.

The basic requirements for the production of a satisfactory joint are:

- The adhesive should exhibit adequate adhesion to the materials involved.
- A two-part epoxy resin with a polyamine-based hardener should be used, which exhibits good moisture resistance and resistance to creep.
- The Tg of the adhesive should generally be greater than 60°C.
- The flexural modulus of the material should fall within the range of 2 to 10 GPa at 20°C.
- The equilibrium water content should not exceed 3% by weight after immersion in distilled water at 20°C. The coefficient of permeability should not exceed 5 x 10-14 m<sup>2</sup>/s.
- It should possess gap-filling properties, be thixotropic, and be suitable for application to vertical and overhead surfaces.
- It should not be sensitive to the alkaline nature of concrete (if present) and its potential effect on the durability of joints.

Adhesive formulations are, in general, complex. To the base resin is added one of a range of different types of curing agents (hardener) and additives, such as fillers, toughening agents, plasticisers surfactants, anti- oxidants and any other required materials. The curing agents are chosen depending upon whether the cure of the resin is to be at ambient or at elevated temperatures; the rate of chemical reaction is approximately doubled for every 8°C rise in temperature. It will be clear that the properties of the adhesive will be altered with the large variety of additives that can be incorporated into the base resin.

If the adhesive is required to join two dissimilar materials, such as polymer composite and concrete or steel, the mechanical and thermal properties should be considered in relation to these two materials. The effects of environmental and other service conditions on the adhesive material and on the behaviour of bonded joints must be considered carefully.

With some bonding surfaces, such as steel, it will generally be necessary to apply an adhesivecompatible primer coat to generate a reliable and reproducible surface. With concrete surfaces it might be advisable to use a primer to enable suitable conditions on which to apply a relatively viscous adhesive. It will not generally be necessary to prime a composite surface.

As with all resins it is necessary to keep a close check on the following items to ensure that the adhesive, when used in the field, is in pristine condition:

- the shelf life is within the manufacturers recommended time limit
- the viscosity and wetting ability is satisfactory
- the curing rate is correct

- the ambient temperature does not fall below the specification value
- post cure is complete before load is applied to the joint.

#### 27.4.3 Elastomers

The elastomer is another member of the polymer family. The material consists of long chain molecules which are coiled and twisted in a random manner and the molecular flexibility is such that the material is able to undergo very large deformations. The material is cross-linked by a process known as vulcanization, which prevents the molecules of the elastomer under load, moving irreversibly relative to each other. After a curing process, the molecules are crossed linked like a thermosetting polymer. As the vulcanization process does not change the form of the coiled molecules but merely prevents them from sliding, the elastomeric material will completely recover its original shape after the removal of an external force.

#### 27.4.4 Geosynthetics

One area of the major advances made by polymers in the last 35 years has been the burgeoning use of these materials in the geotechnical engineering industry. The most commonly known material is the geotextile; a simple definition of a geotextile is a textile material used in a soil environment.

In the early 1970s these materials were referred to as civil engineering fabric or filter fabrics where their primary use was for filter applications. In the latter part of the decade they became known as geotechnical fabrics as they were primarily used in the geotechnical soil engineering applications. It was in the early 1980s that the term geotextile was suggested as a suitable name for this type of material. At the same time impermeable polymeric membranes were also being used increasingly. These materials became known as geomembranes. Thus in the mid 1980s many types of polymeric based materials were being used in the geotechnical engineering industry and many of these could not be classed as either a geotextile or a geomembrane. To encompass all these polymeric materials the new name 'geosynthetic' was derived, which is defined as a synthetic (polymeric) material used in a soil environment. Ingold and Miller (1988) discuss the different materials available for use in civil engineering, their properties and their measurement.

Geosynthetics, which are all thermoplastic polymers, can be divided into five broadly based categories:

- Geotextiles: polymeric textile materials used in geotechnical engineering applications. These materials are essentially permeable to the passage of water.
- Geogrids: open, mesh like polymeric structures.
- Geomembranes: polymeric materials in sheet form which are essentially impermeable to the passage of water.
- Geo-linear elements: long, slender, polymeric materials normally used as reinforcing tendons in soils and rocks.
- Geo-composites: covers all polymeric materials used in a soil environment not covered by the above four categories.

Each of these is now discussed.

#### Geotextiles

Geotextiles are usually classified by their method of manufacture and are made in two stages: the manufacture of the linear elements, such as fibres, tapes, etc. and the fabrication of those linear elements into geotextiles. The fibres are the basic load-bearing elements in the material and the forming technique determines the structure and hence the physical and mechanical characteristics of the system. The main fibres used in geotextiles are the synthetic ones such as polyethylene, polypropylene, polyester and polyamide.

#### Geomembranes

Geomembranes are synthetic materials manufactured in impermeable sheet form from thermoplastic polymers or bituminous materials. Both materials can be reinforced or unreinforced; the former is manufactured on a production line and the latter can be produced on a production line or in situ. The matrix can be reinforced by textiles.

#### Geo-linear elements

Geo-linear elements are long, slender strips or bars consisting of a unidirectional filament fibre core which is made from a polyester, aramid or glass fibre in a polymer sheath of a low-density polyethylene or a resin. The components of the system form a composite, in that the fibre provides the strength and extension characteristics and the matrix protects the fibre from internal influences and provides the bonding characteristics with the soil.

#### Geogrids

Geogrids are often grid-like structures of thermoplastic polymer material, and in conjunction with the soil form a quasi-composite system, where the grid structure is the fibre and the soil is assumed to be the 'matrix' and forms an efficient bond with the fibre. Geogrids are of two forms:

- cross-laid strips;
- punched thermoplastic polymer sheets.

The manufacturing techniques for the strips and polymer sheet are discussed in Hollaway (1993).

#### Geocomposites

Geocomposites consist of two or more different types of thermoplastic polymer systems combined into a hybrid material. Their main function is to form a drainage passage along the side of the water course, with a polymer core as the drainage channel and the geotextile skin as the filter.

As is apparent, many of the materials in each of the above groups are fibre composites of a parent polymer reinforced with polymer fibres and so will be discussed in more detail in the next section.

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#### **Example Questions**

1) Explain the molecular structure and properties of the following polymer types and in addition provide at least one specific example for each case along with a possible application:

- (i) thermoplastic(ii) thermoset
- (iii) elastomer

2) What are the principal processing methods of thermoplastic polymers? Explain in detail the most important method from the civil engineering viewpoint

3) Draw the schematic drawing of a typical creep curve for a polymer under a uniaxial tensile stress

4) Draw the schematic drawings of the mechanical response (stress-strain) of a material at two different times. Consider three cases:

- (i) elastic material
- (ii) liner viscoelastic material
- (iii) non-linear viscoelastic material

5) Explain the time temperature superposition principle (TTSP)

6) Polymers are used widely as engineering adhesives. Explain their advantages for such applications; discuss their use and provide at least two specific civil engineering examples

#### **Further Reading**

#### Books

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#### **Online resources**

- http://www.bpf.co.uk/
- https://connect.innovateuk.org/web/polymers
- http://www.iom3.org/polymer-society/polymer-society-annual-reports
- https://www.ihs.com/products/chemical-market-plastics-polymers-global.html
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- http://www.polymerlink.com/
- http://www.industry-plaza.com/polymers-e398.html
- http://www.plasticproducts.co.uk/
- http://www.fern-plastics.co.uk/

Material	Relative density	Ultimate tensile strength MPa	Modulus of elasticity in tension GPa	Coefficient of linear expansion 10 <sup>-6</sup> / <sup>0</sup> K
<u>Thermosetting</u>				
Polyester	1.28	45-90	2.5-4.0	100-110
Vinylester (BASF Palatel A430-01)	1.07	90	4.0	80
Ероху	1.03	90-110	3.5-7.0	48-85
<u>Thermoplastic</u>				
Polyvinyl Chloride (PVC)	1.37	58.0	2.4-2.8	50
Acrylonitrile butadiene styrene (ABS)	1.05	17-62	0.69-2.82	60-130
Nylon	1.13-1.15	48-83	1.03-2.76	80-150
Polyethylene	0.96	30-35	1.10-1.30	120

 Table 27.1
 Typical mechanical properties for some thermosetting and thermoplastic polymers



Fig. 27.1 (a), The long-chain molecules of a thermoplastic polymer; (b), the attached and/or cross-linked molecules of a thermosetting polymer.



Fig. 27.2 Total creep curve for a polymer under a uniaxial tensile stress



Fig. 27.3 Stress-strain behaviour of elastic and viscoelastic materials at two values of time.



Fig. 27.4 Typical creep curves for a non-linear viscoelastic material for varying stress values. Isostrain stress–log time curve and the build up to isochronous stress–strain curves.



Fig. 27.5 The shift process shown diagrammatically.