

A-Z Encyclopedia Outline

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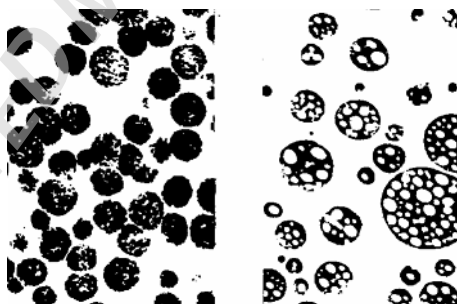
1. Abrasion Resistance

Also known as wear resistance, a characteristic describing the resistance of a material to wear, which takes place via the erosion of small particles from the surface as a result of the frictional forces exerted by a sliding member. A suitable measure of the rate of wear is provided by the ratio V/μ , where V is the volume abraded per unit sliding distance and μ is the coefficient of friction, which corresponds to the amount of abraded substance per unit energy dissipated in sliding. The abrasion resistance is measured in a number of different ways, according to the expected service conditions of a particular product. The most common method is to use abrasive paper mounted on a rotating drum, allowing contact with a specimen subjected to a constant load in order to bring about the formation of debris, which gives rise to loss of material by wear.

2. ABS

A blend or alloy consisting of a glassy styrene–acrylonitrile random copolymer matrix and dispersed microscopic rubbery butadiene–acrylonitrile random copolymer particles, which contain sub-micrometre glassy polymer inclusions. The three letters stand for acrylonitrile, butadiene and styrene. Acrylonitrile–butadiene–styrene (ABS) polymers are produced either by blending a styrene–acrylonitrile (SAN) copolymer (glassy major component) with a butadiene–acrylonitrile rubber (NBR) copolymer (rubbery component), or by a specially designed bulk polymerization method. The latter consists of dissolving the rubbery

component in a mixture of the monomers for the formation of the glassy matrix, followed by free-radical polymerization, which produces the glassy SAN matrix, grafted onto the diene elastomer. At any early stage of the polymerization, there is an inversion of phases, leading to the precipitation of small glassy particles into the diene elastomer, which precipitate into larger particles, forming the characteristic morphological structure of these toughened polymer systems. The different particle structures obtained with the two methods of production are shown in the diagram.



Structure of rubber toughening particles in ABS polymers. Left: System produced by blending of emulsions. Right: System formed by mass polymerization. Source: Schmitt (1979).

There are many grades of ABS available commercially, differing in rigidity characteristics, which are determined by the amount of rubber used, and also in the degree of plasticization of the glassy phase by the elastomer component. The glass transition temperature (T_g) values are in the region of 100–110 °C for the glassy phase and around –40 to –50 °C for the rubbery component. The ordinary polymer grades are opaque, owing to the particle size of the precipitated particles being greater than 1 μm and to the

substantial difference in the refractive index values for the two components.

ABS is widely used in the automotive industry, as it combines its intrinsic high toughness with the ability to produce surfaces with a high gloss, and also because of the ease with which parts can be metallized by conventional electroplating methods. It is also available in the form of blends with polycarbonate, which exhibit better thermal oxidation stability and higher rigidity than conventional ABS grades. (See Styrene polymer.)

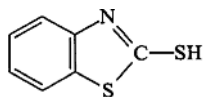
3. Absorbance

A coefficient denoting the fractional intensity of radiation absorbed by a body, that is,

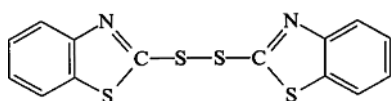
$$\text{absorbance } \alpha = \frac{\text{flux of radiation absorbed}}{\text{total incident flux}}.$$

4. Accelerator

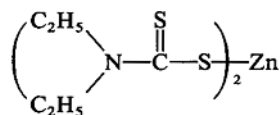
An additive used to speed up the rate of cross-linking reactions in the curing of thermosetting resins or elastomers. For polyester thermosetting resins, the accelerator is usually a cobalt naphthenate or cobalt octoate in solution. For the case of elastomers, the accelerator is a sulfur-containing compound, such as a thiourea, mercaptan and dithiocarbamate, or a non-sulfur-containing compound, such as a urea, guanidine and aldehyde diamine. The chemical structures of typical accelerators for sulfur curing of elastomers are shown.



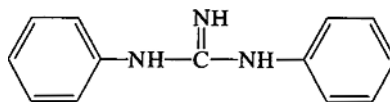
2-mercaptobenzothiazole (MBT)



2,2'-dithiobisbenzothiazole (MBTS)



zinc diethyldithiocarbamate (ZEDC)



diphenylguanidine (DPG)

In many cases, mixtures of accelerators are used to obtain a synergistic effect. Typically, a thiazole type is used with smaller amounts of dithiocarbamate or an amine.

5. Acetal

A term used for poly(methylene oxide) (PMO), represented by the chemical formula $-(CH_2O)_n-$. Acetals are crystalline polymers with a melting point (T_m) in the region of 180–190°C and a T_g around –40°C. They are also available in the form of random copolymers containing small amounts of ethylene oxide units. Acetals are widely used in engineering applications for their high resistance to creep and wear under high loads. They also have a good resistance to solvents and low water absorption characteristics, which makes them suitable for applications requiring dimensional stability under moist environmental conditions. Blends with up to about 30% polyurethane elastomers have been reported to display a good balance of engineering properties with respect to stiffness, strength, toughness and solvent resistance.

6. Acid Number

A term used to denote the acid content of a polymer or resin, which is defined as the amount in milligrams (mg) of KOH (potassium hydroxide) required to neutralize 100 g of polymer or resin.

7. Acoustic Properties

Describe the response of a material to sound and particularly the absorption of sound. In polymers, the absorption of sound takes place through molecular relaxations. The parameter that denotes the capability of a polymer to dissipate mechanical energy through vibrations, known as the loss factor or damping factor ($\tan \delta$), is also used to describe the sound absorption characteristics of polymers. (See Viscoelasticity.) The methods used to measure acoustic properties are broadly divided into wave propagation, resonance and forced vibration methods.

Resonance and forced vibration methods are used to measure the Young's modulus and shear modulus as viscoelastic parameters comprising an elastic and a loss component. Wave propagation methods are used, on the other hand, to record the actual sound absorption characteristics of materials. Measurements are made by sending acoustic pulses with duration less than 1 ms through the specimen immersed in a liquid, and detecting them by another transducer on the opposite surface.

8. Acrylate Elastomer

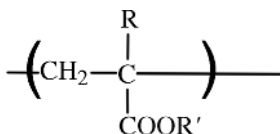
(See Acrylic polymer.)

9. Acrylic

A generic term for monomers and polymers containing acrylate or methacrylate units. (See Acrylic polymer.)

10. Acrylic Polymer

Contains acrylic monomeric units in the molecular chains, represented by the general formula shown.



Polymers where R is an H atom are called polyacrylates, and those where R is a methyl group are called polymethacrylates. Acrylics are generally amorphous polymers and are available as linear polymers or blends (thermoplastic), cross-linkable elastomers and cross-linkable adhesives and surface coatings. The properties of acrylic polymers are strongly dependent on the nature of the substituent R and R' groups, as illustrated in the table.

	Density (g/cm ³)	T _g (°C)
Poly(acrylic acid)	—	106
Poly(methyl acrylate)	1.22	8
Poly(ethyl acrylate)	1.12	−22
Poly(<i>n</i> -butyl acrylate)	<1.08	−54
Poly(<i>t</i> -butyl acrylate)	1.00	43
Poly(methacrylic acid)	—	130
Poly(methyl methacrylate)	1.17	105
Poly(ethyl methacrylate)	1.12	65
Poly(<i>n</i> -butyl methacrylate)	1.06	20
Poly(<i>n</i> -hexyl methacrylate)	1.01	−5
Polyacrylamide	1.30	165

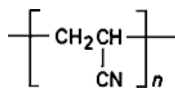
Source: Data from Mascia (1989).

The data in the table clearly illustrate three important aspects of the structure–property relationship in polymers, respectively chain stiffness (energy required to rotate a group attached to the carbon atom in the backbone chain), internal plasticization (creating free volumes between polymer chains) and intermolecular forces. On this basis, one notes that polymethacrylates have a higher T_g than the corresponding acrylates. Increasing the length of the alkyl-group acrylate or methacrylate polymers brings about a large reduction in T_g through internal plasticization. The presence of a

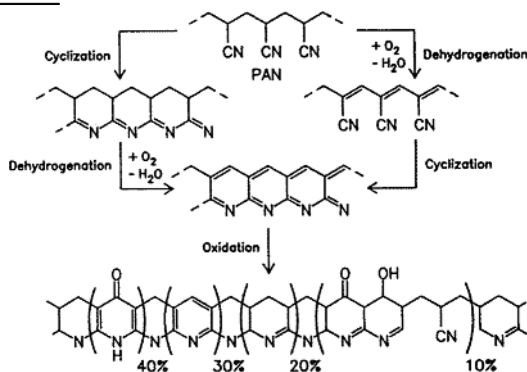
carboxylic acid or an amide group causes the opposite effect through the increase in intermolecular forces by the formation of inter-chain hydrogen bonds. The main characteristics of acrylic polymers available commercially are described below in alphabetical order of the monomer units within the polymer chains.

10.1 Acrylic Elastomer

Generally available as a random copolymer or terpolymer, typically poly(ethyl–butylene acrylate) with T_g within the range -30 to -40°C . These elastomers are well known for their resistance to oils, as well as for their oxidative stability at high temperatures and



where the CN groups are organized in an atactic configuration, preventing the molecular chains from packing in a highly ordered crystalline lattice. The fibres are produced by solution spinning, because of the high viscosity and the rapid decomposition of the polymer at the temperatures that would be required for melt spinning. Thermal degradation takes place by cyclization involving the pendent CN groups along the polymer chains, which results in the formation of infusible ladder polymers, as shown by the reaction scheme, and confers on the fibres a certain degree of fire retardancy



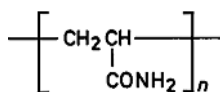
in UV light environment. They tend to absorb large quantities of water via hydrolysis of the ester groups. Vulcanization can be carried out by either peroxide curatives, for systems containing unsaturation in the main chains, or by metal hydroxides through salt formation via carboxylic acid groups.

10.2 Acrylic Adhesive

(See Adhesive.)

10.3 Acrylic Fibre

Produced from polyacrylonitrile (PAN), which is represented by the chemical formula



Moreover, this particular feature makes PAN fibres suitable for the production of carbon fibres due to the dimensional stability that they acquire while they are heated up to the high temperatures required for graphitization. (See Carbon fibre.)

10.4 Acrylic Flocculant and Hydrogel

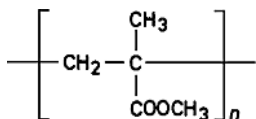
Based on polyacrylamide, a water-soluble crystalline polymer represented by the formula shown.

10.5 Acrylic Impact Modifier

Based on methyl methacrylate–butadiene–styrene (MBS) terpolymer alloys, used widely as impact modifiers in rigid PVC formulations. They are produced mainly from emulsions of a styrene–butadiene rubber (SBR) elastomer and through graft polymerization of methyl methacrylate chemically bonded on the surface of the pre-formed SBR particles. The toughening action in poly(vinyl chloride) (PVC) compounds arises mostly from the miscibility of the acrylic outer layers of the dispersed particles with the PVC matrix. These are preferred to ABS impact modifier systems in applications requiring superior resistance to UV light.

10.6 Acrylic Plastic

The most important polymer in this category is poly(methyl methacrylate) (PMMA), a glassy polymer available either as a thermoplastic material or as a lightly cross-linked pre-formed product, such as sheets or rod castings. PMMA is widely for its high transparency and high resistance to UV light. It is represented by the formula shown and is usually available as a homopolymer grade. (See Acrylic polymer.)



11. Activation Energy

A term in the Arrhenius equation widely used to denote the sensitivity of the rate of chemical or physical processes to changes in temperature. The activation energy (ΔH) is determined from the slope of the plot of the logarithm of the rate of reaction, or rate of physical change, against the reciprocal of

the absolute temperature (T). This can be derived from the Arrhenius equation,

$$\text{rate } K = A \exp(-\Delta H/RT),$$

where A is a constant for the system R is the universal gas constant. (See Arrhenius equation.)

12. Activation Volume

A term in the Eyring equation used to describe the sensitivity of the yield strength of materials to changes in applied strain rate. It is an adaptation of the Arrhenius equation for which the activation energy term (ΔH) is replaced by the term ($\Delta H - v\sigma_Y$), where v is the activation volume and σ_Y is the yield strength. The product $v\sigma_Y$ represents the quantity by which the activation energy has been reduced by the application of the stress required to induce yield (plastic) deformations. (See Yield failure.) The Eyring equation is written as

$$d\varepsilon/dt = B \exp[(\Delta H - v\sigma_Y)/RT],$$

where $d\varepsilon/dt$ is the strain rate used in the test, corresponding also to the rate at which yielding deformations take place, and B is a material constant. (See Eyring equation.)

13. Activator

An additive used in conjunction with an accelerator for the vulcanization of elastomers. Activators consist of metal oxides or salts of lead, zinc or magnesium, often used in conjunction with stearic acid to enhance their solubility in the rubber mix.

14. Addition Polymerization

The conversion of monomer to polymer without the loss of other molecular species. This is contrary to the case of condensation

polymerization, which takes place through the loss of small molecules, such as water. Typically, addition polymerization takes place by a free-radical mechanism or cationic polymerization.

15. Additive

A substance added to a polymer formulation in minor amounts to improve or modify specific characteristics related to manufacture and/or end use of products.

16. Additive Concentrate

A mixture of additive and a polymer powder (usually) where the amount of additive present is much larger than the quantity required in the final formulation. The concentrate is mixed with the neat polymer or resin to bring down the amount of additive to the required level. (See Master batch.)

17. Adherend

A term often used to denote the component in contact with the adhesive layer.

18. Adhesive

Substance used to stick (bond) two or more components of a product or structure. Adhesives can be divided into 'hot-melt adhesives', based on thermoplastic polymers, 'curable adhesives', based on thermosetting resin, and 'pressure-sensitive adhesives', based on elastomeric polymers. Apart from the bonding requirements, any difference in molecular structure or formulation details between polymer compositions used for 'bulk' components and those used for adhesives arises from differences in the way the two systems have to be

processed or applied. The table lists some polymers used for adhesives.

Commercial name	Chemical nature
<i>Thermoplastic hot melts</i>	
Polyesters and polyamides	Low-crystallinity systems
Phenoxy	Poly(glycidyl hydroxyl ether)
EVA	Ethylene-vinyl acetate copolymer
EEA	Ethylene-ethyl acrylate copolymer
<i>Thermosetting (cold cure and heat curable)</i>	
Phenolics	Mostly modified with NBR
Epoxy	Mostly DGEBA resins
Acrylics	Several types available
<i>Pressure-sensitive adhesives (PSAs)</i>	
Most uncured elastomers	Contain tackifiers
<i>Water-borne emulsions</i>	
Poly(vinyl acetate)	Partially hydrolysed

The chemical compositions of polymers used for hot-melt adhesives are similar to those used for plastics, but they have lower molecular weights to meet the low-viscosity requirements for manufacturing purposes. Adhesive grades are usually copolymers containing small amounts of carboxylic acid or hydroxyl groups to enhance their affinity and bonding characteristics for the more common adherends. Oligomeric systems used for curable adhesives usually contain complex mixtures of auxiliary ingredients, and often have a heterogeneous morphology, as a means of obtaining a good balance of properties and also to satisfy specific requirements for a multitude of applications. Acrylic adhesives are usually based on low-volatility monomers containing peroxide initiators with a very long half-life. Some very innovative systems have been developed that take advantage of prevailing conditions to accelerate or induce curing in

the adhesive. An interesting example is the anionic polymerization of cyanoacrylate adhesives, which takes advantage of the slightly basic nature of many inorganic substrates and the presence of water adsorbed on the surface to promote cure reactions within the adhesives.

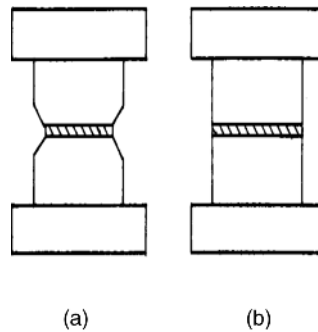
19. Adhesive Test

Usually refers to a mechanical test for measuring the strength of bonded specimens, which is normally defined as the force required to separate the adherends of a joint, divided by the overall bonded area. Under ideal conditions, that is, those in which the actual intrinsic strength of the adhesive is to be measured, failure has to take place within the bulk of the adhesive (cohesive failure) and not at the interface between adherend and adhesive (interface failure). This is an essential requirement of structural adhesive, and it is for this reason that the surface of the adherend is often treated to increase the interfacial bond strength to the level required to ensure that failure takes place within the adhesive. The preparation of the surface of the adherend usually entails the generation of chemical groups that can react with the adhesive to produce chemical bonds across the interface. If the adhesive is mechanically strong (i.e. it requires high stresses for fracture), it is unlikely that cohesive failures can be achieved only through physical bonds at the interface, even when these are strong types such as hydrogen bonds, bearing in mind that these may be weakened through the absorption of

water. Nevertheless, the strength values obtained depend on geometric factors, such as the dimensions of the bonded area and the thickness of the adhesive layer. Consequently, they cannot be used as fundamental parameters for use in theoretically based design procedures and have to be considered primarily as data for 'quality control and specifications'.

19.1 Tensile Test

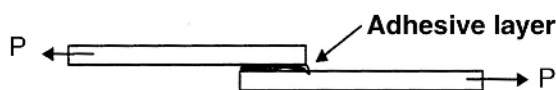
Typical bonded specimens, known as butt joints, are shown. These are pulled at constant strain rate up to fracture. The bond strength is calculated by dividing the load to fracture over the bonded area.



Typical axial loaded 'butt-joint' specimens: (a) wood-to-wood bond; (b) metal-to-metal bond.

19.2 Shear Test

Also known as 'lap shear' to describe the type of specimen used. Typical specimens types are shown.



(a) Single lap shear



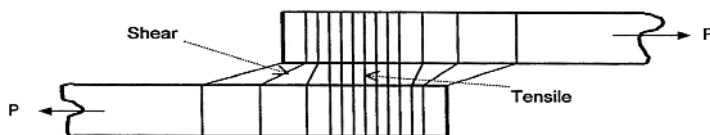
(b) Aligned lap shear

These are the more widely used tests, mainly because both the specimens and the experimental procedure are simple. The strength of the bonded specimen, known as the 'lap shear strength', is expressed as the load to fracture divided by the bonded area. In these tests the adhesive layer is subjected to a combination of tensile and shear stresses at the interface and within the adhesive layer, which vary in the opposite manner along the bonded length of the lapped area, as shown. The shear stress in the adhesive layer decreases from a maximum at the edge of the lapped area to zero in the middle when the bond line is sufficiently long. Completely the opposite to this is the change in axial tensile stress, which is maximum in the centre and smallest (zero) at the outer edges.

cantilever specimens. These are specimens with a very long bond line subjected to a 'crack opening' fracture mode by pulling the bonded cantilevers away from each other and recording the load during fracture propagation along the 'bonded line'. The value of the critical strain energy release rate G_c is calculated from a fundamentally derived equation, using the appropriate values for dC/da (i.e. the rate of increase of specimen compliance C with crack length a). (See Compliance and Fracture mechanics.)

Two types of specimens are usually used:

- the uniform double cantilever beam (UDCB) specimen, which is known also as the thin strip test;
- the tapered double cantilever beam (TDCB) specimen, which is known also as the wedged specimen.



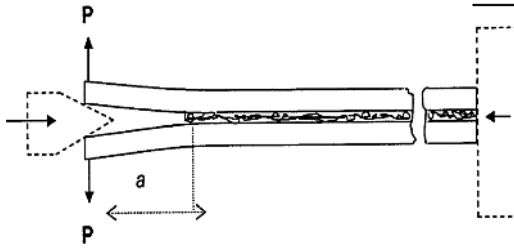
Variation of strain in the adhesive layer and the two adherends in a single lap shear test.

19.3 Fracture Toughness Test: General

The fracture toughness of bonded specimens is normally measured using double

The description and geometry of these two specimen types are given below.

19.4 Fracture Toughness Test: UDCB Specimen



Double cantilever beam (thin strip) test. The load can be applied either directly at the edge of the strips or through a wedge at the open end of the bonded strips.

In UDCB testing, it is important that the two adherends undergo only elastic deformation during the test to ensure that all the energy imposed is used only to induce fracture of the adhesive layer. Note that, for a double cantilever beam, the compliance C is given by the expression

$$C = \frac{\Delta}{P} = \frac{64a^3}{EWB^3},$$

where Δ is the deflection, P is the load, a is the non-bonded distance (cf. crack length), E is the Young's modulus of the adherend, W is the width of the specimen and B is the thickness of the beam. Differentiating the above equation with respect to a gives an expression for dC/da that can be substituted in the generic equation for G_c , which can then be calculated from the recorded load to fracture (P_f), that is, the maximum load recorded in the test. From the above equation one obtains

$$G_c = \frac{96P_f^2 a^2}{EW^2 B^3}.$$

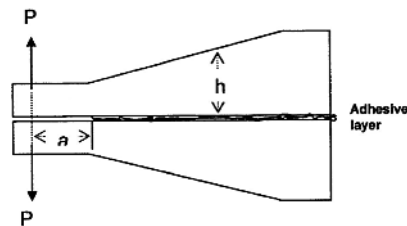
Note that, when the adherend is very flexible (compliant), the test is known as the 'T-peel test'. If, on the other hand, one of the adherends is very rigid (i.e. very thick and/or the material has a very high modulus) and the other is very compliant (i.e. very thin and/or the material has a very low modulus), the test is known as the 'L-peel test'. Both tests can be used to measure the

fracture toughness in terms of the G_c value, which is given by the formula

$$G_c = (P_f/B)(1 + \varepsilon),$$

where B is the width of the flexible adherend strip and ε is the tensile strain ($\varepsilon = P/BWE$). When ε is very small, the value of G_c is obtained directly from the ratio P_f/B . The unit N/m corresponding to this ratio is equal to J/m², which is the appropriate unit for G_c .

19.5 Fracture Toughness Test: TDCB Specimen



Tapered double cantilever specimen for fracture toughness testing of adhesives.

For TDCB specimens the value of dC/da is given by the expression

$$dC/da = 6m/EB,$$

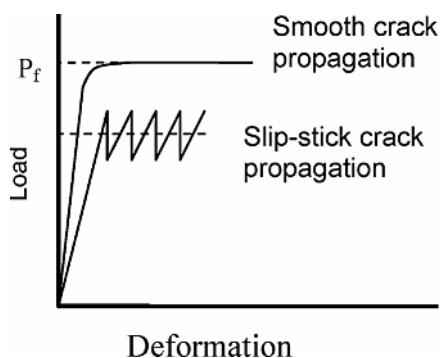
where B is the thickness, E is the Young's modulus of the beam and m is a function of both the height h of the beam and crack length a , that is, $mh^3 - (1 + \nu)h^2 - 4a^2 = 0$,

where ν is the Poisson ratio of the beam. The taper of the outer edge of the specimen is estimated by maintaining the value of m constant so that the height (depth) of the beam becomes larger as the non-bonded (crack) length increases. The solution of m gives a slightly concave contour for the outer edge, with the curvature becoming more pronounced as the non-bonded distance gets smaller. Therefore, by using large values of a , the contour of the specimen becomes approximately linear, that is, the gradient is constant. Typically, if the gradient angle is 11° , then

$$dC/da = 90/EBh_0,$$

where h_0 is the height (depth) of the beam at the crack tip. This simpler geometry makes it easier to produce specimens for testing. The advantage of the TDCB specimen is that the fracture load (P_f) remains constant during fracture propagation, making it possible to measure the rate of crack propagation along the bond line.

A slip-stick type of crack propagation occurs if fracture takes place in a mixed mode, involving cleavage through the bulk of the adhesive layer and debonding at the interface with the adherend.



Typical force–deformation curves obtained in tests with TDCB specimens.

The TDCB test is particularly useful for fractures induced under fatigue (cyclic loading) conditions, so that the crack growth rate

can be measured as a function of the frequency and magnitude of the applied load. Using UDCB specimens, on the other hand, the load to fracture decreases after crack initiation because the value of dC/da becomes smaller with increasing crack length. For many systems, the fracture toughness of structural adhesives has been measured also with respect to the long-term static and dynamic (fatigue) behaviour, through measurements of the increase in crack length with time and/or loading cycles.

20. Adhesive Wetting

Wettability is an essential characteristic of an adhesive to ensure that it completely covers the surface of the adherend. This condition is satisfied by ensuring that the adhesive and adherend have a similar surface energy. In quantitative terms, this requirement is to make sure that the so-called ‘work of adhesion’, W_A , is very small. This is related to the surface energies, γ , between the various phases by the equation

$$W_A = \gamma_{LV} + \gamma_{SV} + \gamma_{LS},$$

where the subscripts LV, SV and LS denote the three interfaces concerned, respectively liquid–vapour, solid–vapour and liquid–solid. The surface energy for the solid–liquid interface is lowest when the respective surface energies of the solid (substrate) and the liquid (adhesive) are very similar. Surface energies depend on the chemical constitution. Low polarity will give low values for the surface energy. Polytetrafluoroethylene (PTFE) has the lowest surface energy because of the absence of net dipoles in the structure. Polyethylene (PE) also has a very low surface energy, owing to the absence of net dipoles, but it is not as low as for PTFE. Polymers with very strong dipoles, such as those containing COOH or OH side groups or NH groups in the main chains

(e.g. polyamides and polyurethanes), have very high surface energies. (See Surface energy.) Surface oxidation of PE or PTFE can introduce polar groups and increase accordingly the surface energy. These treatments would be used, therefore, to improve the bonding of polar adhesives, such as those based on epoxy resins. Chemical reactions across the interface bring about an increase in the interfacial bonding between adhesive and adherend, which represents the highest level of bonding that can be achieved.

21. Adiabatic Heating

A term used to describe the self-heating of a polymer taking place during intensive mixing and extrusion, resulting from the shearing action of the rotors of the mixer or the screw of an extruder.

22. Air-Slip Forming

A technique used in vacuum forming (also thermoforming) by which air is injected through fine orifices in the cavity of the mould in order to prevent sticking and rapid cooling of the polymer sheet during drawing. (See Thermoforming.)

23. Aliphatic

A term used in chemistry to describe the linear connection of carbon atoms to each other. This implies the absence of benzene rings, a compound containing which would be referred to as 'aromatic'. (See Aliphatic polymer.)

24. Aliphatic Polymer

A polymer containing aliphatic carbon atoms along the backbone of the molecular chains, for example, polypropylene.

25. Alkyd

A type of polyester resin. The term is derived from a combination of the words alcohol and acid to indicate that it is a product resulting from the reaction of an alcohol (multifunctional) and a dicarboxylic acid. The latter is usually a mixture of naturally occurring fatty acids and aromatic types. Alkyds are normally divided into oxidizing and non-oxidizing types. The oxidizing types are produced from unsaturated fatty acids, whose double bonds can react with oxygen from the atmosphere to produce free-radical species that can cause cross-linking reactions. The non-oxidizing types are cross-linked by reactions of the free OH groups in the chains with a urea formaldehyde or melamine formaldehyde resin, or with multifunctional isocyanates.

26. Allophonate

A type of chemical group formed from reaction between an isocyanate and a urethane group.

27. Alloy

(See Polymer blend.)

28. Alpha Transition Temperature

The alpha (α) transition temperature T_α is thermodynamically classified as a secondary transition, denoting the temperature at which the first partial derivative of a primary function, such as the volume or the enthalpy ($\partial V/\partial T$ or $\partial H/\partial T$), shows a discontinuity. T_α is also known as the glass transition temperature (T_g) insofar as it represents a reference temperature for the change in the deformational behaviour of a polymer from the glassy state to the rubbery state, which

entails a reduction in modulus by a factor of 10^3 – 10^4 with increasing temperature.

29. Alternating Current (AC)

A current resulting from the application of a cyclic (sinusoidal) voltage. The cyclic variation of voltage and current takes place at specific frequencies. (See Dielectric properties.)

30. Aluminium Trihydrate $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$

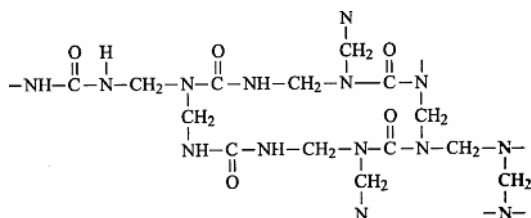
A functional filler used to impart flame-retardant and antitracking characteristics to a polymer. Particle size is in the range 2–20 μm and surface area in the region of 0.1–6 m^2/g . The amount of water corresponds to 34.5 wt%, which volatilizes very rapidly above 220 °C and reaches about 80% completion at around 300 °C. (See Flame retardant, Antitracking and Filler.)

31. Amine-Terminated Butadiene–Acrylonitrile (ATBN)

An oligomer, also known as liquid rubber, amine-terminated butadiene–acrylonitrile (ATBN) is used for the toughening of epoxy resins. Commercial systems are available with molecular weight between 2000 and 5000 and with acrylonitrile content around 25–35%. (See Epoxy resin, subsection ‘Reactive toughening modifiers’.)

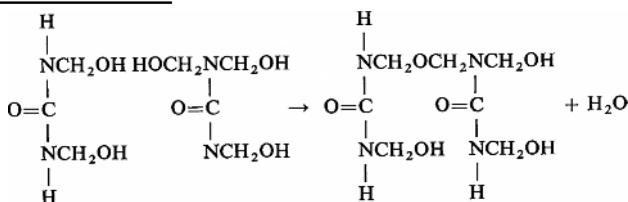
32. Amino Resin

A resin produced from the reaction of a multifunctional amine and formaldehyde. The most commercially important amino resins are urea formaldehyde (UF) and melamine formaldehyde (MF) resins. Both resins are water clear, unlike phenol formaldehyde (PF) systems. The network structure of the cured UF resins and the reactions involved are shown schematically.



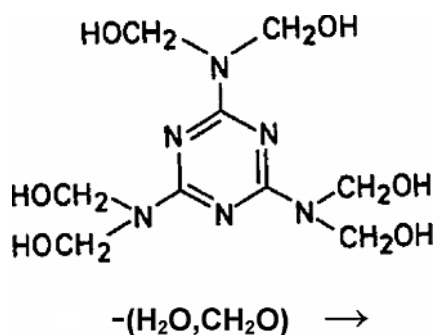
Dense network structure of cured urea formaldehyde (UF) resin.

These are formed from condensation reactions between $-\text{CH}_2\text{OH}$ of the basic resin to produce oxymethylene bridges, as shown in the scheme.

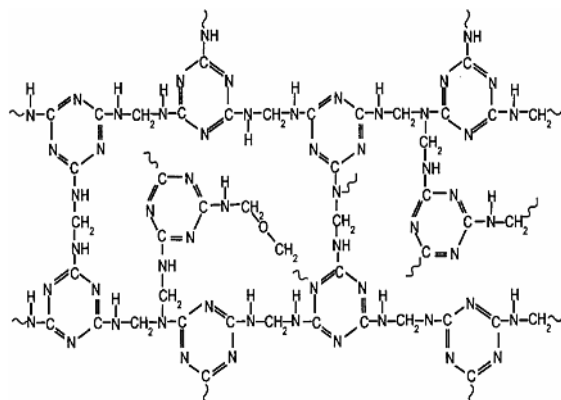


Condensation reactions in the curing of UF resins.

Similar reactions take place in the cross-linking of MF resins, as shown.



A large number of these oxymethylene bridges undergo a loss of formaldehyde to produce a denser network.



Network of a highly cross-linked melamine formaldehyde (MF) resin. Source: Ehrenstein (2001).

The moulding compounds of both UF and MF resins contain cellulose fillers and additives, such as pigments, curing catalysts, external lubricants and sometimes also small amounts of plasticizer. For white formulations, the cellulose filler is usually a bleached variety in order to eliminate the possibility of producing undesirable tints from impurities. Sometimes MF resins are butylated in order to increase their shelf-life when used as aqueous solutions or micro-suspensions. In this case the condensation reactions will be preceded by the loss of butanol. For both UF and MF resins, however, the curing reactions rarely go to

completion, so that there will be a substantial number of CH_2OH groups present in addition to $-\text{NCH}_2-\text{O}-\text{CH}_2\text{N}-$ and $-\text{NCH}_2\text{N}-$ groups.

The use of cellulosic fillers for moulding powder or paper for laminates not only provides an efficient reinforcing and toughening function but also ensures that the water produced does not result in the formation of voids. The strong affinity of water with the structural units of amine resins, via hydrogen bonds, allows a substantial amount of water to remain dissolved in the network.

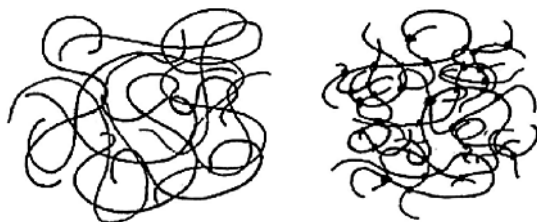
33. Amnesia

A term (jargon) used in the technology of heat-shrinkable polymers to denote the extent by which the product fails to reach the dimensions it had before being stretched. (See Permanent set.)

34. Amorphous Polymer

The term is used to denote the lack of order at the supramolecular level. This implies

that the molecular chains (thermoplastics) or the macromolecular networks (thermosets or cross-linked rubber) have a random configuration, as illustrated in the schematic diagram.



Linear polymers (left) and cross-linked polymers (right).

Step 3. Termination: Polymer chains reach full size when the monomer is exhausted or through secondary reactions with other species present, such as solvent.

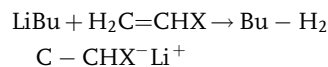
35. Anatase

A crystalline form of titanium dioxide (titania) used as the basic component of white pigments. (See Titanium dioxide.)

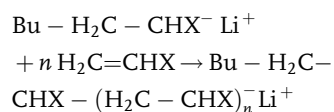
36. Anionic Polymerization

A type of polymerization that takes place via the growth of chains containing an anion in equilibrium with a small-sized counter-ion (cation) originating from the initiator, usually a metal alkyl (e.g. lithium butyl) or an alkyl metalamide (e.g. potassamide). The steps involved in the polymerization are as follows.

Step 1. Initiation: Addition of the anion from the initiator onto the monomer,



Step 2. Propagation: Rapid addition of a large number of monomer molecules,



37. Anionic Surfactant

(See Surfactant.)

38. Anisotropic

A product or specimen exhibiting anisotropy. (See Anisotropy.)

39. Anisotropy

The characteristic of a specimen or product in which the value of a given property is different in magnitude when measured in two perpendicular directions. In the case of cylindrical geometries such as rods, fibres or tubes, the two perpendicular directions of anisotropic behaviour are the longitudinal and circumferential directions. Anisotropy in polymer products results from the preferential alignment of polymer chains and crystallites in a specific direction. In most cases anisotropy is deliberately introduced to enhance the properties in one specific direction. In the case of fibres and tapes, the orientation is deliberately induced in the axial, or longitudinal, direction as a means of increasing the mechanical strength in the direction in which the product would be subjected to mechanical forces in

service. (See Orientation.) In the case of composites, anisotropy arises from the different degree of fibre alignment in two perpendicular directions.

40. Annealing

A term denoting the thermal treatment (usually at constant temperature followed by slow cooling) of a specimen or product with a view to releasing the internal stresses set up during moulding or to developing the highest possible degree of crystallinity. This thermal treatment serves also to stabilize the dimensions and properties of a product prior to it being used in service. Annealing is carried out at temperatures very close to the glass transition temperature (T_g value) of the polymer if amorphous or just below its melting point (T_m) if the polymer is crystalline. Note, however, that annealing may induce embrittlement of products made from glassy polymers through physical ageing and those made from crystalline polymers through the thickening of the lamellae.

41. Anodizing

(See Metallization.)

42. Antiageing

(See Antioxidant, Stabilizer and UV stabilizer.)

43. Antibacterial Agent

(See Antifouling additive and Antimicrobial agent.)

44. Antiblocking Agent

An additive that produces roughness on the surfaces of a soft polymer product, prevent-

ing these from sticking to another through interfacial attraction forces. This phenomenon is particularly problematic in the case of flexible films used for plastic bags, as it makes it difficult to open them. The most widely used antiblocking additives consist of fine particles 20–50 nm diameter, usually inorganic fillers such as silica, talc, kaolin, calcium carbonate and zeolites.

45. Antidegradant

A generic name used primarily in relation to rubber formulations to denote an additive that improves the resistance to ageing. (See Degradation and Stabilizer.)

46. Antifoaming Agent

An additive used to prevent the formation of foams during the mixing of liquid systems. They are also known as defoamers or foam suppressants. Early systems were primarily vegetable or mineral oils. Nowadays antifoaming agents are complex mixtures in the form of hydrophobic solids containing active ingredients, consisting of a variety of compounds derived from water-soluble polymers. They normally contain a liquid-phase component such as mineral or vegetable oils, poly(ethylene glycol), silicone oils (polydimethylsiloxanes) and fluorosilicones (polytrifluoropropylmethylsiloxanes). These are particularly effective in non-aqueous system particles because of their low surface energy and immiscibility. The other component is a solid consisting of hydrophobic silica or hydrocarbon waxes. Antifoaming agents may also contain ancillary ingredients consisting of surfactants, coupling agents, stabilizers and carriers. The latter have the function of holding the ingredients together. In general, the defoamer has a surface energy lower than that of the foaming medium and should be immiscible and

readily dispersible. The main uses of defoamers in polymer systems are in coating, latex and emulsion formulations.

47. Antifouling Additive

Known also as biocides and bactericides, these contain chemicals that are toxic to microorganisms. These include zinc and barium salts, as well as mixtures of zinc oxide or barium metaborate with thiazoles or imidazole compounds. They are widely used for marine coatings. More recently, extensive use has been made of the incorporation of sub-micrometre particles of silver, particularly for furniture and appliances for clinical application. (See Antimicrobial agent.)

48. Antimicrobial Agent (Biocidal Agent)

An additive with the ability to inhibit the growth of a broad range of microbes, such as bacteria, moulds, fungi, viruses and yeasts. Antimicrobial activity in polymers can be attained either by the incorporation of additives or through modifications of the chemical structure. Additives that can be used as antimicrobial agents include antibiotics, heavy-metal ions (silver or copper), cationic surfactants (quaternary ammonium salts with long hydrocarbon chains), phenols and oxidizing agents. An additive that is frequently used as an antimicrobial agent in polymers is metallic silver, in the form of fine (nano-sized) particles, even though it does not release metal ions as easily as copper. The use of copper is avoided, however, as it can have some devastating effects on the heat stability of the polymer. In order to increase the rate of release of ions, silver salts are sometimes embedded in hydrophilic carrier particles, such as silver-substituted zeolites. Macromolecular antimicrobial agents used in

polymers include poly(2-*t*-butylaminoethyl methacrylate) (PTBAEMA) and N-halamines grafted onto polymer chains through acid or anhydride functionalization of the latter. N-halamines are compounds in which one chlorine atom is attached to the nitrogen atom. In both cases the antimicrobial activity derives from the formation of a quaternary ammonium salt, while the polymeric nature prevents them from being easily extracted by water.

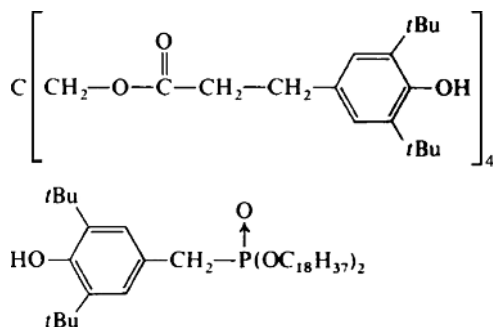
49. Antimony Oxide

Corresponds to Sb_2O_3 and is used as a white pigment as a result of its high scattering power resulting from its high density (5.7 g/cm^3) and as a functional filler in conjunction with chlorinated or brominated compounds to impart fire-retardant characteristics to polymers. Optimal tinting and flame-retardant properties are achieved with particle size in the range of 0.2 to $1 \mu\text{m}$. These systems are generally considered to produce toxic products under burning conditions. (See Flame retardant.)

50. Antioxidant

An additive within the general class of anti-ageing additives or stabilizers. An antioxidant reduces the rate of degradation of polymers resulting from the action of oxygen in the atmosphere on defective sites of a molecular chain. This creates free radicals, which initiate and propagate a series of reactions resulting in chain scission, cross-linking and formation of oxygen-containing chromophore groups, such as carbonyls. These reactions cause discolorations and embrittlement of the product. An antioxidant reacts with the free radicals to produce inert compounds, thereby preventing the propagation of degradation reactions. The antioxidant activity is regenerated

through secondary reactions so that they can act as efficient stabilizers even at very low concentrations (0.1–0.5%). Typical antioxidants used in polymers are *ortho*- and *para*-substituted tertiary butyl phenols or aromatic amines. Amine antioxidants are less widely used, as they impart a dark discoloration to the products and they are rather toxic, which makes them less attractive for general uses. Typical examples of phenolic stabilizers are shown.



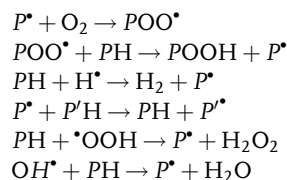
Example of phenolic antioxidants.

Note that the second example of phenolic antioxidant contains a phosphite group, which provides a synergistic effect with the phenolic unit by acting as a peroxide decomposer. The more common types of antioxidants do not have a built-in peroxide decomposer and, therefore, they require the presence of another additive to exert this function. These are typically phosphite and mercaptan compounds, which accelerate the decomposition of hydroperoxides and deactivates them through the formation of stable products.

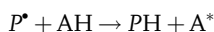
Antioxidants intervene in the degradation reactions caused by the formation of free radicals in the polymer chains (P) through a series of reactions with oxygen, starting at sites with the weakest CH bond, such as tertiary or allylic carbons. The 'initiation' reaction.



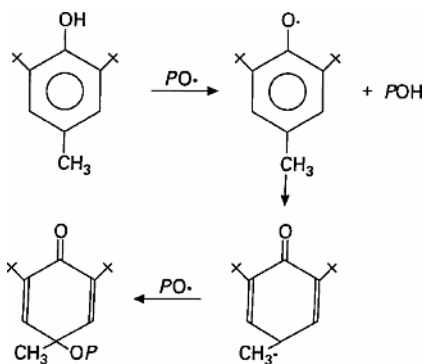
is followed by rapid propagation reactions



Propagation reactions are the most damaging reactions insofar as they affect a large number of polymer molecules. The antioxidant intervenes predominantly at this stage by reacting with the free radicals in the polymer chains, forming non-reactive products, a phenomenon known as quenching. Denoting by AH the antioxidant molecule, either amine or phenol type, the quenching reaction can be written as

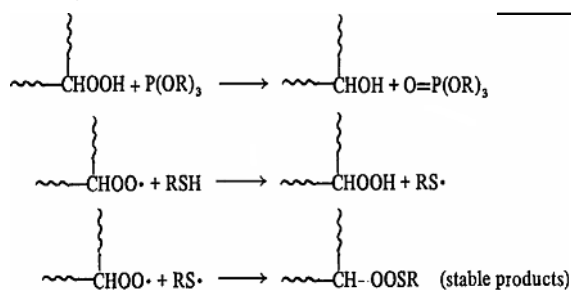


where A^\bullet represents a stable (non-reactive) radical. The mechanism for the loss of reactivity of the A^\bullet radicals for the case of a phenolic antioxidants is as shown.

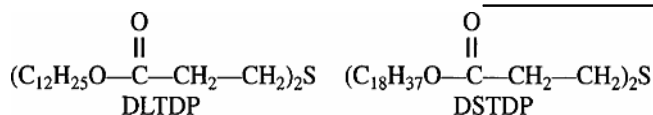


Note that the stability of the radicals is due to internal delocalization, making it inaccessible for interacting with polymer chains.

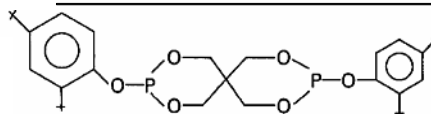
The reaction scheme for the action of secondary stabilizers as peroxide decomposers is:



Examples of mercaptan and phosphite compounds used as secondary stabilizers are dilaurylthiodipropionate (DLTDP) and distearylthiodipropionate (DSTDTP).



The structures of two phosphite secondary stabilizers are shown. These are known commercially as Weston 618 (left) and Ultrinox 626 (right).



51. Antiozonant

An additive used primarily in diene elastomers to improve the resistance to attack from ozone in the environment, particularly the ozone generated in electrical motors and other devices through corona discharges. An antiozonant is often a wax capable of migrating to the surface to form an oxidation-resistant layer.

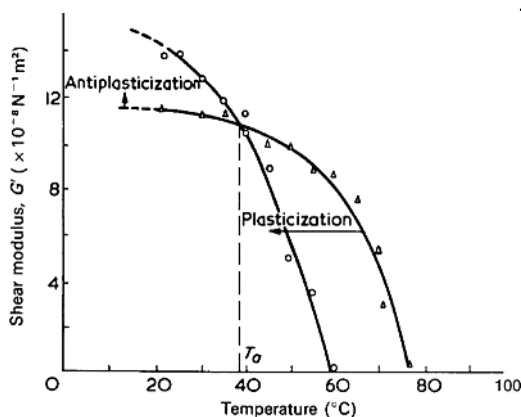
52. Antiplasticization

Although the term denotes a phenomenon with the opposite effect to plasticization,

this must not be interpreted in terms of an increase in the glass transition temperature. Antiplasticization is a phenomenon that brings about an increase in modulus at low temperatures, as well as embrittlement at

ambient temperatures. In PVC, this is brought about by the incorporation of small amounts of plasticizers (typically 5–10 parts per hundred) capable of exerting strong physical interaction, such as H– bonds with the Cl atoms in the chains. These interactions cause a depression of short-range relaxations, normally associated with rotational movements of side groups in a polymer chain. The effects of the addition of

small amounts of plasticizer in PVC compounds on the variation of modulus with temperature, shown in the diagram, provides evidence that antiplasticization is essentially a phenomenon occurring at low temperatures and that normal plasticization takes places at higher temperatures.



Plot of dynamic shear modulus against temperature for a PVC sample (curve on the right, triangles) and a sample containing 9 wt% tricresyl phosphate (curve on the left, circles). Source: Mascia (1978).

53. Antistatic Agent

An additive used in polymer formulations to reduce the build-up of static charges on the surface of products or structures. Antistatic agents are additives capable of migrat-

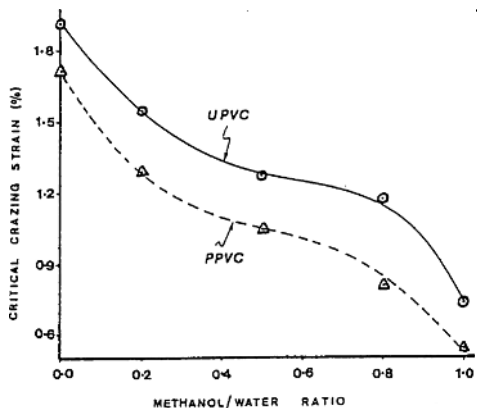


Illustration of effects of antiplasticization of a PVC compound. Upper curve: unplasticized PVC. Lower curve: PVC plasticized with 9 wt% tricresyl phosphate. Source: Mascia et al. (1989).

ing to the surface of a product, forming a conductive path through ionization resulting from the absorption of moisture in the

atmosphere. These are usually surfactants consisting of long-chain aliphatic amines, amides or quaternary ammonium salts, alkyl aryl sulfonates and alkyl hydrogenphosphates. Among other compounds used as antistatic agents are water-soluble ionically conductive polymeric compounds, such as hexadecyl ethers of poly(ethylene glycol). (See Surface resistivity.)

54. Antitracking

Preventing the formation of surface tracks on the surface of a dielectric, or insulator, subjected to a high voltage. The surface tracks consist of carbonaceous paths that are formed as a result of the chemical degradation of the polymer, thereby producing very conductive channels capable of leaking a current to ground. Tracking of insulators is often prevented by depositing suitable oils or greases on the surface, such as silicone types, as they are thermally stable and do not form carbonaceous residues.

55. Antitracking Additive

An additive that imparts antitracking characteristics to a polymer. These are substances that can release large quantities of water when the outer surface layers of the insulator reach temperatures in the region of 300–400 °C, as a result of the heat produced by the arcs generated by the applied high voltage. Arcs contain very reactive oxygen ions, which give rise to extremely rapid degradation reactions. The most widely used antitracking additive is aluminium trihydrate, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, which loses all three H_2O molecules at around 350 °C, corresponding to about 35 wt% weight loss. (See Flame retardant.)

56. Apparent Shear Rate

The shear rate calculated on the basis that the polymer melt behaves as a Newtonian liquid. The value of the apparent shear rate, $\dot{\gamma}_a$, at the wall can be calculated from the flow rate Q and the dimensions of the channels, as follows.

- **Circular channel:** $\dot{\gamma}_a = 4Q/\pi R^3$, where R is the radius of the channel.
- **Rectangular channel:** $\dot{\gamma}_a = 6Q/WH^2$, where W is the width of the channel and H is the depth, valid for shallow channels, that is, when $W \gg H$.

A shape factor, S , has to be introduced for other situations. Correction has to be made by multiplying the value calculated from the above equation by the appropriate shape factor, $S = 1 - 0.65(H/W)$. (See True shear rate and Non-Newtonian behaviour.)

57. Apparent Viscosity

The value of the viscosity (η_a) calculated on the basis that the polymer melt behaves as a Newtonian liquid, that is $\eta_a = \tau/\dot{\gamma}_a$, where τ is the shear stress and $\dot{\gamma}_a$ is the value of the apparent shear rate.

58. Aprotic Polar Solvent

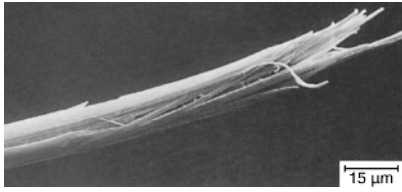
A solvent without the capability of undergoing hydrogen-bonding interactions through the involvement of protons.

59. Araldite

A tradename for a variety of epoxy resins.

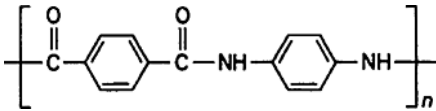
60. Aramid

A term used to denote aromatic polyamide fibres, an example of which is shown.



Example of an aramid fibre displaying fibrillation characteristics. Source: Ehrenstein (2001).

The chemical structure of a typical polyamide used for the production of aramid fibre is shown.



These are often identified by the trade-name Kevlar. The molecular chains of aromatic polyamides are very rigid and are oriented in the axial direction of the fibres, forming strong attractions with other neighbouring molecules via hydrogen bonds. This provides a high strength and modulus, with a high level of ductility, relative to carbon fibres (which are extremely brittle) and even glass fibres. Aramids have a very high melting point (around 500 °C) but are susceptible to UV-induced degradation. (See Composite.)

61. Aromatic Anhydride

Frequently used compounds for the production of polyesters and polyimides and sometimes used as curing agents for epoxy resins.

62. Arrhenius Equation

The name of an equation derived by the chemist Arrhenius to describe the variation of the rate of a chemical reaction (K) as a

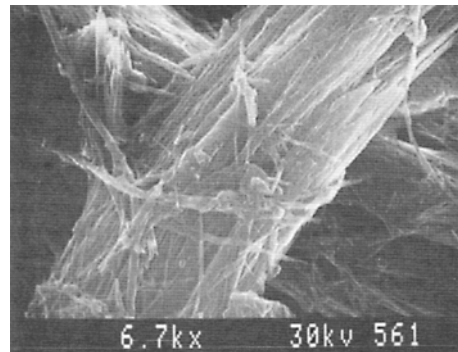
function of the absolute temperature (T). This is written as

$$K = A \exp(-\Delta E/RT),$$

where A is a characteristic constant, ΔE is the activation energy for the reaction and R is the universal gas constant. This equation has been found to apply equally well to physical processes that involve movements of some structural constituents, for instance in the case of electronic or ionic conduction and gas diffusion.

63. Asbestos

A magnesium silicate fibre occurring naturally in four different forms. The 'chrysotile' variety has been used for reinforcement of thermosetting resins, particularly phenolic types, in engineering applications such as brake pads. It consists of fine fibrils packed into bundles for its high reinforcing efficiency due to the high modulus (see the micrograph).



SEM micrograph of chrysotile asbestos fibres. Source: Wypych (1993).

Owing to toxicity issues, asbestos has been largely replaced by other high-performance reinforcing fibres. (See Composite.)

64. Aspect Ratio

The ratio of the length to diameter of fibres used in composites. Sometimes used also

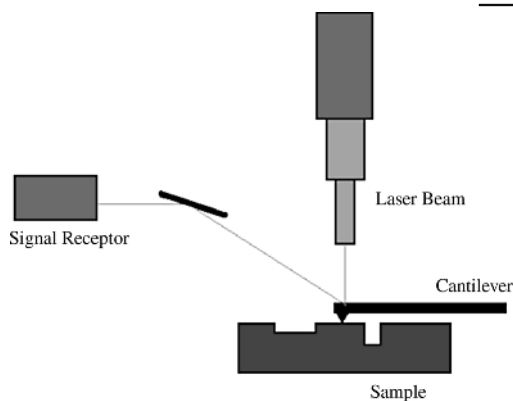
for platelet particles as the ratio of the nominal width to the thickness.

65. Atactic Polymer

A term used to denote the lack of a specific order in the chemical structure of a polymer, such as polypropylene. A polymer with an atactic chemical structure. (See Isotactic polymer and Tacticity.)

66. Atomic Force Microscopy (AFM)

A microscopic technique that produces images of the surface topology via the tip of a scanning probe that measures the atomic forces (attractive or repulsive) against the surface under examination. Atomic force microscopy (AFM) is particularly useful for examining surface features of very small dimensions, for example 10–1000 nm. The tip is placed on a cantilever that will deflect as a result of the atomic surface forces, as shown in the diagram.



Schematic diagram of the operating principle of an atomic force microscope. Source: Lavorgna (2009).

proximity with the surface without touching it. In most cases a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the surface of the sample.

67. Attenuated Total Reflectance Spectroscopy (ATR Spectroscopy)

An infrared spectroscopy technique used to identify specific chemical groups present on the surface of a sample, supported on a prism with a very high refractive index, which reflects the incident infrared radiation transmitted through the thin film in contact with the prism. (See Infrared spectroscopy.)

68. Attenuation

(See Damping.)

69. Avrami Equation

The movements are detected by the reflection of a suitable focused laser beam. In tapping-mode AFM the cantilever is oscillated at a certain frequency with an amplitude that allows the tip to come into close

Originally developed to model the crystallization rate of metals during solidification, it has been found to apply equally well to the

crystallization of polymers. The Avrami equation is usually written as

$$\ln(1-\varphi_t) = Zt^n,$$

where φ_t is the volume fraction of polymer crystals (also known as the degree of crystallinity) at time t , while Z and n are characteristic constants for the polymer.

70. a/W Ratio

The ratio of the length of the crack (or notch), a , to the width of the specimen,

W , used in the evaluation of the toughness of materials using fracture mechanics principles. (See Fracture mechanics.)

71. Azeotropic Copolymerization

Conditions in which the composition of the molecular chains of a copolymer (i.e. the ratio and position of the two monomer units) remains the same throughout the polymerization process.