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SUMMARY OF INTRODUCTORY LECTURES

on

CHEMISTRY AND PHYSICS OF PLASTICS[1]

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The main scope of these lectures is to give an overall picture of polymer science and to discuss the correlations between the chemical structures of the different plastics materials and physical properties. Furthermore it will be shown that any sensible applications of plastics materials depend on the exact knowledge of the changes of the properties with temperature, time, etc.

Taking into account time periods (up to 1880, 1880-1910, 1910-1920; 1920-1930, 1930-1940; 1940-1960, 1960-) the historical development of polymer science will be shown.

A great number of different plastic-materials which are now on the market will be discussed concerning their chemical structure, their manufacturing processes as well as their applications. This theoretical part will be supplemented by a great number of slides and original samples.

Typical examples of three different ways to build up macromolecules (high polymers) will be fairly well explained:

a) Polymerization (chemical reactions in which the molecules of monomers (low molecular weight compounds) are linked together to form molecules of high molecular weight. In a restricted sense these are the chemical reactions in which monomers containing carbon-carbon unsaturated bonds are linked together to form polymers.)

b) Polycondensation (reactions in which molecules of monomers are linked together with the elimination of water or other simple molecules.)

c) Polyaddition (in a restricted sense chemical reactions in which polymers are formed by additions of monomers other than those containing carbon-carbon unsaturated bonds involving hydride transfer.)

Besides analytical methods which are well known (elementary analysis, atomic ratios, mean molecular weight) a brief survey of the most important and modern methods (mass spectrometry, vapour phase chromatography, thermogravimetry, differential thermoanalysis, X-ray structure analysis, infrared spectroscopy, electron spin and nuclear magnetic resonance) will be given. Since three of these methods

(vapour phase chromatography, differential thermo analysis and infrared spectroscopy) are used at all modern laboratories, it will be shown to which extent these analytical methods can help to gain important results. Practical experiments will be carried out.

The reasons for the well-known subdivision of plastics into

a) "elastomers" (materials that at room temperature can be stretched repeatedly to at least twice their original length and, upon immediate release of the stress, will return with force to their approximate original length),

b) "thermoplastics" (materials capable during processing of being repeatedly softened by increase of temperature and hardened by decrease of temperature) and

c) "thermosetting plastics" (materials capable of being changed into substantially insoluble, infusible, crosslinked products, when cured by heat or by other means such as radiation catalysts etc.)

will be explained. The "amorphous", "semi-crystalline" and "crystalline" state of order will be discussed.

Furthermore the physical meaning of the two important transition points will be explained:

a) glass transition temperature
This temperature characterises the transition of amorphous and semi-crystalline polymers from their solid state to a viscous or rubbery one or vice versa. This transition generally occurs over a relatively narrow temperature region and is similar to the solidification of a liquid to a glassy state; it is not a phase transition. Not only do hardness and brittleness undergo rapid changes in this temperature region but other properties such as thermal expansion and specific heat also change rapidly.

b) melting-temperature
This is the temperature which characterises the transition of semi-crystalline or crystalline polymers from their rubbery or viscous state in the former case and from the solid state in the latter case to a liquid state or vice versa.

It will be demonstrated which structural parameters account for change in glass transition temperature as well as melting temperature. Finally, it will be shown in which way the two characteristic temperatures mentioned above change if copolymers (these are polymers in which two or more chemically non-identical monomeric units are present in irregular or unknown sequence) or polyblends (physical mixtures of structurally different homo- or copolymers) are considered.

The methods available and normally used to determine

a) particle size,
b) particle size distribution and
c) molecular size distribution

will be described.

The important influence of molecular weight (degree of polymerisation) on the properties will be discussed. Special attention will be drawn to the correlation between molecular weight and tensile strength. The physical meaning of a generally valid but empirical equation will be explained. The fundamental difference between weight average and number average molecular weight will be discussed. Also the factor of nonuniformity will be mentioned. Furthermore the different possibilities to determine mean molecular weights of high polymeric materials will be described (light scattering, osmotic pressure, ultracentrifuge, sedimentation, diffusion, viscosity).

Based on data of polyolefines established empirically but nevertheless useful in practice will be mentioned and discussed:

a) the correlation between molecular weight and molecular weight distribution,
b) the correlation between molecular weight (molecular weight distribution) and crystallinity,
c) the correlation between molecular weight dictribution and linearity of the macromolecules,
d) the correlation between chemical structure and degree of crystallinity and
e) the correlation between stereoregularity and state of order.

Then density (specific volume) and temperature dependence as a criterion of

a) thermal expansion,

b) glass transition temperature as well as melting temperature and

c) degree of crystallinity

will be considered.

Refractive index (usually determined at 20°C and with monochromatic light of wavelength 5892 Å) will be mentioned because with its help a quick qualitative determination of an unknown plastic material can be made. From the values of refractive index at two different wavelengths (4861 and 6563 Å) the optical dispersion can be calculated.

From the thermal properties specific heat (the quantity of heat which must be supplied to the mass unit of a material in order to raise its temperature by one degree), thermal conductivity (the rate of heat flow under steady conditions through unit area per unit temperature gradient in the direction perpendicular to the area) and coefficients of linear as well as of cubic thermal expansion (the former being the reversible change in length of a material per unit length per degree change in temperature and the latter being the reversible change in volume of a material per volume unit per degree change in temperature) will be discussed and the important differences to the traditional materials illustrated. Attention will also be given to the temperature dependence of the thermal properties. Furthermore correlations between chemical structure and temperature of decomposition as well as temperature of deflexion under load (the temperature at which a specimen submitted to a given bending stress and heated according to a specific temperature programme reaches a certain deflexion) and Vicat softening point (the temperature at which a standard flattened needle under a specified load and a uniform rate of temperature rise penetrates a specimen to a defined depth) will be shown.

Another group of properties to be fairly well discussed is water absorption, water vapour absorption, water vapour transmission, as well as gas permeability and gas diffusion.

Special attention will be given to the electrical properties of plastics materials. In this respect dielectric constant (the ratio of capacitance of a capacitor in which the space between and around the electrodes is entirely and exclusively filled with the insulating material in question to the capacitance of the same configuration of electrodes in vacuum), dielectric dissipation factor (the tangent of the loss angle by which the phase shift between current and voltage of a condenser filled by the respective material deviates from $\pi/2$), surface resistivity (it is the electric potential gradient parallel to the direction of the current flow along its surface divided by the current per unit width of surface), volume resistivity (it is the electrical potential gradient parallel to the direction of the current flow in the material divided by the current density), dielectric strength (it is the property of a dielectric which opposes a disruptive discharge), arc resistance (on the surface of the specimen between two electrodes an electric arc is produced by alternating current whose power and duration are increased in a specified manner), breakdown voltage (the voltage necessary to produce a disruptive discharge between two conductors (electrodes separated by the specimen) and tracking (this is the formation of a carbonized conducting path across the surface of an insulating material between electrodes maintained at a given potential difference) will be theoretically explained and the measurements of these properties demonstrated in practice.

One part of the introductory lectures is based on a detailed discussion of viscosity. Therefore viscosity coefficient, viscosity number (reduced viscosity) and limiting viscosity number (intrinsic viscosity) will be explained. Furthermore melt index (the amount (in grams) of a fused thermoplastic material which is pressed under standardized temperature and pressure conditions through a sprue or orifice of specified dimension within ten minutes) will be discussed and its measurement demonstrated.

An essential part of the lectures will be concentrated on the mechanical properties:

Ball indentation hardness (Rockwell hardness)

The indentation depth of a steel ball of standard size pressed under standard conditions on the surface of the specimen. The ball indentation hardness is the quotient of the load and the area of the spherical indentation. The Rockwell hardness is expressed in scale units.

Compressive strength

The ability of a material to withstand compressive stress.

Deformation under load by compression

The compression of a specimen effected by load and expressed in % of the initial height of the specimen.

Modulus of elasticity in compression

Flexural strength

The ability of a material to withstand flexural stress

Flexural stress at a given deflexion

In case of materials showing under load a marked creep the flexural stress at a given deflexion is measured instead of the flexural stress at break.

Flexural yield strength

The stress at a point on a load-deflexion curve at which the load does not increase with an increase in deflexion.

Modulus of elasticity in flexion

Tensile strength

The ability of a material to withstand tensile stress.

Elongation at maximum load

Elongation of a specimen at the moment at which the stress-strain curve reaches the maximum tensile stress.

Elongation at break

Elongation during the tensile test just before the specimen breaks.

Modulus of elasticity in tension

Tear resistance

The ability of a material (film) to withstand tearing. It is a complex function of its ultimate resistance to rupture.

Tear propagation resistance

The ability of a material to withstand a propagation of an existing single slit or nick until rupture of the specimen.

Impact strength

The ability of a material to withstand shock loading. In practice three different test methods are used.

a) Impact test (Charpy)
b) Impact test (Izod)
c) Falling ball test.

Torsional shear strength

The ability of a material to withstand torsional shear stress. The shear strength is calculated from the maximum load during a shear or torsion test and is based on the original cross-section area of the specimen.

Logarithmic decrement of mechanical damping

In case of oscillating deformations the logarithmic decrement of mechanical damping is the natural logarithm of the ratio of two subsequent amplitudes of oscillation.

Torsional modulus

Stress-strain curve

A diagram in which corresponding values of stress and strain are plotted against each other.

a) Dependence on thickness of specimen
b) Dependence on strain rate

Tangent modulus

The slope of the stress-strain curve at any specified stress or strain.

Secant modulus

The slope of the secant drawn from the origin to any specified point on the stress-strain curve.

Yield point

The lowest stress in a material and less than the maximum attainable stress, at which an increase in strain occurs without an increase in stress.

Point of rupture

Cold flow (creep)

The slow deformation of a stressed material at temperatures within the working range of the material:

a) Dependence on load
b) Dependence on temperature
c) Dependence on time

Instantaneous recovery in creep

The decrease in strain occurring immediately upon unloading a specimen before any creep recovery takes place.

Creep recovery

The time-dependent portion of the decrease in strain following unloading of a specimen.

Creep strength

The stress that causes a given creep in a given time in a given environment.

Fatigue

The process of progressive localized permanent structural change occurring in a material subjected to fluctuating stresses and strains which may culminate in cracks or complete fracture.

Fatigue life

The number of cycles of stress or strain of a specified character that a given specimen sustains before failure of a specified nature occurs.

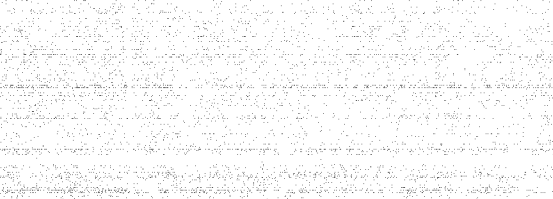
Fatigue limit

The limiting value of the median fatigue strength if the number of cycles becomes very large.

For the sake of completeness it should be mentioned that this part is by no means a theoretical one, because several instructive experiments will be performed.

Special attention will be drawn to resistance to cold, resistance to heat (the highest temperature which a material can temporarily or permanently withstand without appreciable deterioration of its properties), light resistance, artificial and natural weathering and ageing.

Under the influence of fire the behaviour of plastics is affected by numerous outside factors and by some specific properties of the materials. The correlation between chemical structure and temperature of thermal decomposition with evolution of flammable gases will be explained. Finally experiments concerning inflammability, burning rate, self-ignition temperature and incandescence resistance will be made.



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