المواد المتراكبة البوليمرية

Composite Polymetric Materials

د. جليل رهيف عكال

المحاضرة الاولى:

Composite Materials:

A composite is a combined materials by the synthetic assembly of two or more components. Certain filler or reinforced agent, and a compatible matrix binder are normally selected inorder to obtain specific properties.

There are three fields of producing composites which are:

1. Metal-matrix composites.
2. Ceramic-matrix composites.
3. Polymer-matrix composites.

We will deal with the 3rd one. The physical properties of polymers can be enhanced by the addition of suitable fillers.

Polymers:

Are good heat and electrical insulations,very poor conductors. The aim of producing composites is to get new polymeric materials with modified properties; physical,chemical,electrical,mechanical,thermal,magnetic,flame-retardation……etc.

Composites are called Engineering materials because of the new properties that they have.They are better than metals due to their properties (out door); e.g. resisting acids, bases, moisture, heat, corrosion, …etc.

They are created to give new specific and selected properties for selected purposes. Composites generally formed from:

Matrix + Binder + Filler

Engineering Materials:

used in construction of building, vehicles, engines, textiles, paper, rubbergoods and household articles of all kinds.

The rapid growth of engg. Materials is due to :

1. The basic raw materials for their production are available in large quantities and are inexpensive (oil,petrol, natural gas, cellulose, starch, adhesires….etc.).
2. The success of intensive research during the past 50 years to find the mechanism of the reactions, also the development to get large scale industrial operations.
3. Today there exist many continous automatics, rapid and expensive methods for spinning, casting, blowing,injection and compression molding.
4. The large no. of available monomers and polymers and copolymers have provided us with continous spectrum of composition and structure of organic macromolecules(Tailor-making approach in synthesis).

Why composite materials ?

1. The need for new materials,having characteristic properties; light-weight high performance engg.plastics are ousting metals in many applications.
2. The continuity of development and increasing sophistication of technology, and the claim for higher standard of living people.

Engg. Materials or composites depend on the supply of basic resins and synthetic elastomers obtained from petrochemicals.

The actual use of composites is in :

- Transportation.
- Marine.
- Construction.
- Corrosion-resistance.
- Electrical& electronics appliance.
- Bussinessequipments.
- Aircraft and Aerospace components.
- In a no. of miscellaneous applications.

The first man-made composites based upon polymers was in about 5000 B.C. in the middle east, where pitch was used as a binder for reeds & boat-building.

How to form composites ?

Any polymer contains some form of additives, ranging from small fractions of catalyst residue to large scale incorporation of say a mineral filler can be called a composite material.

The most important additives are those introduced for some specific purposes & would include fillers, plasticizers, colorants, reinforeing fibers, blowing agents, stabilizers against sun light, flame retardants,processing acid & a final group of miscellaneous addition.

Generally

Composite polymers are multiphase materials of two or more components in which the polymer form the continous phase, can be considered as containing fillers or reinforcing agents, the function of the two are frequently overlapping. Also they can be considered as materials of two separate origins, physically produced by dispersing one phase (filler) in a continous matrix (polymer).

Fillers for Polymers

OrganicInorganic

-Wood flour -Glass,Silica

-Starch -$CaCO_3$,Clays

-Carbon, Carbonblack -Al_2O_3,TiO_3,Sb_2O_3

-Protein -Fe_2O_3,Mgo,ZnO

-Cellulose -Asbestos,Boron

-Nylons,…etc. -Metals,…etc.

Fillers can change shape during formulation.Fillers have low density, cheap extrudores for more expensive base polymers, they are available, reducing the cost of articles & producing modified properties.

Type of fillersPurpose

Metal Powders To increase electrical and thermal conductivity, high density and radiation resistance, sound absorbers.

Pigments Colorants

e.g.TiO_3,Fe-oxides,

carbon black, Azo-dyes,

Mn,Pb-chromate.

Fibrous fillers To increase thestrength,

Stiffness & thermal stability.

Glass fibers Reinforcing agents they are the

most reinforcing for polymers

(GRP) to improve the mechanical

Properties.

How to select fillers ?

According to :

1. Primary Properties:
   a- The particle; size,distribution,shape.
   b- Surface area,surface modifiers.
   c- Particle Packing.
   d- Chem-composition,reactivity…..
2. Secondary properties:
   a- Optical.b.Thermal. c.Physical. d.Electrical.
   e.Rheology. f. Chemical.

Factors leading to good polymer-filler bonding:

1. Low contact angle between polymer & filler.
2. Low viscosity of resin & time of application.
3. Increasing pressure to assist flow.
4. High viscosity after application (curing,cooling,…..).
5. Clean & dust-free surface on filler.
6. Resin less rigid than filler.
7. Simmilar thermal expansion coet.
8. A propirate design (specific to intended application).

Coupling agents

Are certain additives used to be as the most important way of modifying filler surfaces inorder to get an improved interaction between polymer&filler,e.g; silan coupling.

Processes to get composites

Compounding

The essential step in the fabrication of good quality products, preparing the polymer system for its find moding procedure.

Three stages:

a-Premixing

b- Dispersion

c-Final shaping

For solid compounding, the basic techniques:

a- Internal mixing-------> Blades.

b- Milling ---------> Roll mills.
c- Extrusion-------> Extruders.

Fabrication

Processing, using moulding pressure or compression moulding.

(Final use step)

Polymer blends

To get composites also.

المحاضرة الثانية:

Inorganic Elements in Polymers

Polymers are organic materials derived from petroleum or living things. Low cost starting materials are available from the petrochemicals industry.

The aim of composites is to convert such materials to a broad range of products with a wide variety of properties.

Organic polymers are light in weight, resistant to corrosion andeasily fabricated into useful objects at moderato temperatures. Most of them are excellent insulators.

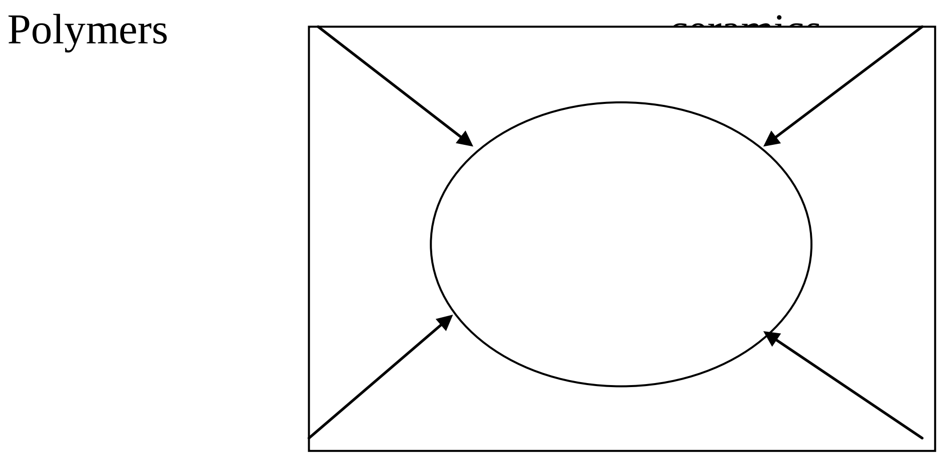
Few organic polymers can be heated for prolonged periods above 150 C^o without either melting or decomposition occurs, it usually results from the reaction of the carbon atoms with atmospheric O_2.

Many polymers dissolve or swell in hot organic liquids or lubricating oils,or hydraulic fluids, and for this reason can not be used in advanced engineering applications. Few organic polymers are useful at both low and high temperatures because of their flexible and or rubbery properties.(e.g. low temps.in high-flying air craft) creat serious hazards, as in space shuttle challenger exploded shortly after liftoff because an O-ring failed, probably because of low temperature embrittlement.

Another example for applications for which no suitable polymers have yet been found; prolonged resistance to UV radiation is essential, in the textile industry where flame – retardant fabrics are needed, and in medicin for the fabrication of artificial organs that will not lead to blood clotting or other undesirable effects.

These are some of the reasons why increasing number of polymer chemists have been exploring the possibility that the replacement of carbon atoms in polymers by inorganic elements may expand the range of properties and overcome some of the disadvantages.

The logic behind this thinking is illustrated in the following Fig. which explain the relationships and connection between four main classes of materials.



Organic polymers are one of the four main types of “Materials”. The other three are ceramic, metals and a wide range of inorganic semiconductor and optical materials.

Ceramic are complicated inorganic systems in which three- dimensional covalently crosslinked “Ultrastractures” coexist with linear inorganic chains & crystalline domains. Most ceramics are made by the high-temperature processing of mineralogical silicates,siliconcarbide,silicon nitride or related inorganic species.

Metals are tough and ductile and have high temperature behavior (but not good as ceramic).Most metals are good conductors of electricity.

On the other hand, they are heavy, pron to corrosion, and require large amounts of energy for their isolation from minerals & for their fabrications.

The fourth class of materials includes the classical semiconductor like Si or Ga arsenide, superconductors, & a variety of optical &electrooptical glasses, all of which are based on the inorganic elements.

However, most of these materials are expensive to produce, difficult to fabricate, & are relatively fragile.

Each of these four types of materials have advantage & disadvantages not shared by the other three. Thus, it seems likely that hybrid systems should be accessible that combine the advantages of all four, while, at the same time, minimizing the disadvantages.

There are three levels to produce inorganic polymers (use inorg. Elements to modify polymers) which are :

1. Inorganic elements can be incorporated into the side groups of an organic polymers.This is perhaps the simplest approach in sense that the synthesis methods of organic polymer chemistry can still be used.

   e.g. the presencebof a transition metal organometallic unit in the side group could give rise to catalytic properties, not found in the parantpolymer.Simillyary, a flame-retardant might impart flame resistance.

2. The inrcorporation of inorganic elements into the backbone of polymer molecules either together with skeletal carbon or without any carbon being present in the skeleton at all.
3. The inorganic-organic polymers are considered to be specifically designed to serve as precursors to ceramics. Polymer of this type haveinorg. elements in the skeleton and either inorganic or organic side groups that react at high temp. to form a covalently crosslinked ultrastructure. Thes are the so called “pre-ceramic”. Polymers that are used as precursors to boron-nitride (BN), silicon nitride, silicon carbide, or even to silicates or alumino-silicates.

المحاضرة الثالثـــة:

Principles of Filler Selection and Use:

Fillers have been considered, especially by their manufacturer, to be cheap extenders or diluents.

Primary properties of fillers:

1. The particle :Filler selection is determined by the partice size distribution, the particle shape &, as a consequence of both, the manner in which the particles pack together.
2. Surface area : Many effects of fillers are surface area dependent, particulary where surfactants, dispersants,surface modifiers polar polymers,…..etc. are sorbed by or reacted with filler surfaces.
3. Particle packing: depends on the determined void vols. Of specific size ranges of uniformly shaped particles.
4. Chem.Composition: chemical reactivity is the chief concern of filler users. Reactivity is a surface effect due to composition.

Secondary Properties of fillers:

1. Optical : Color is an obvious property of fillers, but is frequently misunderstood.Particles reflect light, as well as refract or bent light, according to their sizes.
2. Thermal: e.g. Thermal conductivity, specific heat, thermophysical effects, & thermochemical effects.

3. Physical: e.g. Density; effects the economics of comp. ozites (Porous or cellular fillers ……).Hardness; Porosity or sorptivness.
4. Chemical: All metallic bonds produce excellent electrical conductivity, whereas ionic & covalent bonds produce nonconductors.Some materials have mixed bonds ionic & metallic produce semiconductors.

Systemic effect of fillers.

1. Economics : Use of fillers is usually to reduce the cost of a compound.
2. Physical :
   - a- Modulus : The must prominent phys. Effect of fillers is the stiffersing, or modulus increase, which they cause in composites.
   - b- Tensile strength: Fillers effect tensile properties according to their packing characteristics, sizes,& interfacial bonding.
   - c- Flexural strength : Fillers reduce flexural strength in proportion to their relative packing volumes.
   - d- Elongation
   - e- Tear resistance :Filler-matrix bonding in flexible composites.
   - f- Impact strength.
   - g- Compressive strength : applied only to rigid matrials.
   - h- Creep & Stress relaxation: Creep is a viscoelastic property.Fillersinc.the relative viscosity, &, as expected, reduce the degree of creep or deformation over a period of time for an applied initial stress.
   - i- Hardness : a measure of elasticity.
   - j- Coefficient of friction.
   - k- Abrasion resistance.
3. Rheological : (Science of flow). Effected by :

a. Filler conc. b. Dispersion c. Intrinsic Viscosity.

4. Chemical : Includes:
   a. Corrosion resistance.
   b. Permeance : Solid, inorg fillers reduce the permeability of plastics to ligs.& gases.
   c. Interface : surface reactivity of the fillers.
   d. Impurities : causing undesirable reactions with polymers & additives.
      Impurities also affect the stability to oxidation, temperature, UV., ….etc .
5. Thermal :
   a. Coeff. of thermal expansion.
   b. Deflection temp.
   c. Thermal conductivity.
   d. Specific heat.
   e. Fire retardancy.
6. Optical :
   a. Color. b. Refrective Index.
7. Electrical :
   a. Dielectric const. b. Dielectric strength.
   b. Arc resistance.d.General electrical.

Properties : Since most organic polymers are covalently bonded, thrir elect. Properties will be v. good.

Many minerals fillers are ionic & covalent bonded; both generate nonconductors, only metallic bonded materials provide free es which readily transport electricity.

Selecting the filler to fit the need.

- Fillers are classified according to commercial fillers, according to the use; Improve the properties,langely dispersion & bonding.
- Lubricating fillers; e.g. molybolenum disulfide, graphile,andteflon.
- Magnetic fillers are black iron oxide, powdered iron or shot,& barium & strontium ferrites.
- Elect. Applications ; fused silica from high purity silica.
- Reduce the thermal expansion of composites; e.g: Li-Al-silicates (has a negative coeff.of expansion= -8 x 10^{-6}).

Optimizing the selection of fillers :

1. Cost reduction.
2. Physical properties improvement .
3. Thermal properties modification-conductivity, sp. Heat.
4. Electrical properties modification: most polymers have excellent properties & superior to fillers.
5. Special requirements. e.g :
   - Reduction of IR transmittancs.
   - Sound reflectance, …..etc.

Mechanical Properties of Composites :

The most important properties for polymers are the mechanical properties.

- Whatever the reason for the choice of a particular polymer for some applications; whedher thermal, electrical or even aesthetic ground, it must still have certain characteristics of shape rigidity & strength.
- The most common way of recording mechanical properties is to carry out stress- strain or load-extension.

- The presence of impurities or low m.wt. additives such as, moisture or organic liquids, will produce a softening as well as weakening, effect.
- Temperature also effects the mechanical properties.

Friction & wear of Composites

In many ways this topic should have been included under the heading of the mech. prop. of polymers, but as it has some rather special aspects, it is considered here. There are two main areas of interest. The first concern the use of polymers & composites in low- friction applications as in bearings & gears, whilst the other in high-friction applicatios such as in brakes &cluches, with tyres being an intermediate case, & a very important one (the annual material wear of tyres is of the order of 10^6tonnes; 1982).

Friction is concerned with the force which opposes movement between two surfaces & has elements of static, kinetic,& rolling friction.

Chemical properties

Although the presence of fillers may have an influence on the prepn. of polymers , talk for example causing a slight dec. in the rate of the free radical polymn. of styrene, with zinc oxide giving a slight inc., and carbon behaving as an inhibitor.

The fillers have an ability to reduce curing exotherms, in polyester crosslinking. Advantage of this is taken either to maintain a low temp. for reaction, or to permit the reaction to be carried out at higher temps.,& so accelerate curing, than would otherwise be possible.

المحاضرة الرابعة :

Nanochemistry

This term appeared in the cited literature at the end of the 1990s .This direction is being explored very rapidly. It is a new, actively developing scientific direction.

Nanochem. Has its own subject, objects for studying, and experimental methods, the analysis of which forms the major subject.

The chief reason of studying nanoparticles of various elements in Periodic table opens up new directions in chemistry that can not be described interms of already known relationships. Particlees less than 1nm , e.g. metals contain less than 10 atoms.

Nanochem : is defined as the field that studies synthesis , Properties, and reactivity of particles & assemblies they form, which measure less than 10nm.

At least in on direction . NC deals with one-, two and three- dimentioned objects such as films, wires and tubes. Particles of nanometer sizes began to attract the attention of scientist in differ fields of science. Nano is derived from the Greek word “nano” which mean small used as the prefix for one billionth part of meter (10^{-9}m).

The last 15-20 years. At present, the programs of many Russian & international congress,conferences, and symposia include the subjects;

Nanoparticles,Nanoclusters, Nanocomposites, Nanotechnology, either as such or as constituents of the section subject.

Nanotechnology

N.T. is one of the evolving and promosing technologies for the new millennium. It is believed to be the potential to become the key technology.

N.T. can be defined as the creation processing, characterization and utilization of materials, devices & systems with dimensions on the order of 0.1-100nm, exhibiting novel&significantly enhanced physical,chemical& biological properties due to their nanoscale size.

N.T. combines knowledge from chemistry, physics,biology, medicine & engineering. Nanometerials can be classified into 0D,1D,2D&3D nanomaterials. Dimensions play a major role in determining the characteristics of nanomaterials including physical, chemical & biological characteristics.

Smaller dimensions nanomaterials have higher surface area compared to 3Dnanomaterials. Recently 2D nanomaterials are extensively investigated for electronic, biomedical, delivery biosensor application,..,etc. with the decrease in dimensions, an increase in surface to volume ratio is observed.

Nanotechnology is now recognized as one of the most promosing areas for technological development in the 21st century. In material research, the development of polymer nanocoposites is rapidly emerging as a multidisciplinary research activity whose results could broaden the applications of polymers to the great benefit of many different industries.

Nanocomposites

N.Cs are materials of the 21st century in view of possessing design uniqueness and property combinations that are not found in conventional composites.

N.C. is defined such that the size of the matrix or reinforcement (filler or additive) falls within the nanoscale. The physical properties and performance of the N.C.will greatly differ from those of the component materials.

N.C. materials have extensive applications in the fields of science,engineeringand medicine.

Nanocompositesare :

1. Lighter in weight.   2. Eco-friendly.   3. Bio-degradable.

4.Cost-effective.   5. Performance-oriented.

6.Suited for diverse applications.

How to achieve these function ?

Is by using organic and natural materials as filler in different polymer blends.

Polymer blends worldwide market volume is estimated to be more than 700,000 metric tons / year (growth 6-7%).

The polymer blending offers possibility of adjusting the cost-performance balance and tailoring the technology to make products for specific and use applications, enhancing resin's performance, improving specific properties.viz. impact strength, solvent resistance,…etc.

The blends help to get :

1. Higher surface area.
2. Aspect ratio which could improve adhesion between nanoparticles and polymers.
3. Lower the amount of loading to a chieve equivalent properties.
4. Provide means for industrial and consumer plastic waste recycling.

Majority of the engg.Nanocomposites materials consists of thermoset epoxy matrix reinforced with continuous glass fiber.

It is well known that polymer-clay nanocomposites could offer better mechanical,thermal and physical properties compared to conventional composites. The polymer nanocomposites(PNC) are polymer(thermosets,thermoplastics,or elastomers) that have been reinforced with small quantities (< 5%) by weight of nano-sized particles having high aspect ratios.

PNC_S represent a radical alternative to conventional filled polymers or polymer blends. The value of PNC_S technology is not only based on the mechanical enhancement of the neat reisn nor the direct replacement of current filler or blend technology. Rather its importance comes from providing value-added properties not present in the neat resin, without sacrificing the resin's inherent processibility& mechanical properties, or by adding excessive weight. PNC_S contain substantially less filler

(1-5% vol) & thus enabling greater retention of the inherent processibility, and toughness of the neat resin.