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Porous Particle-Polymer Composites

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1. Introduction

Composite materials designed to retain porosity usually have pore-structure specific application. Common man-made materials that exploit porosity include paper coatings, superconductors, nano-silicates and hydroxyapatite. Typical characteristics sought after include; capabilities of mass transfer and liquid retention, improved opacity, lighter weight, enhanced gloss, controlled spread and imbibition, and control of heat conduction. Though required for the enhancement of specific properties, porosity also has the drawback of reducing mechanical strength and stiffness. This chapter serves as an introduction to porous particulate-based composites. Included are the physical properties of minerals and their raw sources for excavation. Also described are the structures of packed particles and the physics of polymer spreading and dispersion. When combined, these effectively govern the geometrical characteristics of the resulting pore structures. Variations in polymer structure that arise through the presence and influence of particles are also explained. Following this section is a review on surface science, adsorption and wetting and the mechanisms of adhesion. To conclude the chapter, is a short discussion on the environmental footprint of particle-polymer composites such as are commonly designed to retain porosity. The primary focus in this chapter is on mineral-particle polymer-matrix composites with porosity.

2. Common mineral particles found in porous composites

This section introduces mineral particles oft used in porous composites. The particulate families of interest are the calcium carbonates, the kaolins, the talcs and the titanium dioxides.

2.1 Calcium carbonates

Calcium carbonates ($CaCO_3$) exist naturally in different forms. There are three crystal structures (aragonite, calcite and vaterite) though calcite, with a rhombohedral structure, is the most commonly used. Substantial calcite deposits can be found around the world. What differentiates chalk from limestone and marble (sources of calcite) are the levels of pressure and temperature to which they have been exposed. When calcite is close to the surface of the earth, a method of surface mining called “quarrying” is used. Otherwise, “underground mining” is used to extract calcite sources. The surface of calcite is reactive to acids, especially stearic acid, which improves its dispersion in polymers. Dispersed calcites usually have enhanced hydrophobic properties as compared to un-dispersed equivalents. Stearic acid molecules react with carboxylate ions and organic chains on the surface of the calcite. Typical uses of calcium carbonates include rubber and plastic applications and they are predominantly utilised for financial benefit. Calcites are widely used in paper as a filling agent and as the main component of paper coatings. The typical types of calcium carbonates used are ground calcium carbonates (GCC) and precipitated calcium carbonates (PCC). PCC requires a three stage chemical conversion. The first is calcination, $CaCO_3$ + heat → $CaO + CO_2$; which is followed by hydration, $CaO + H_2O \rightarrow Ca(OH)_2$; and the final stage is the precipitation, $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ (Kemperl 2009).

2.2 Kaolins

Kaolin (Clays) ($Al_2O_3.2SiO_2.2H_2O$) are high aspect ratio particles with both anionic and cationic surface properties. Close to a thousand deposits are still commercially mined. The most noteworthy resources are in Cornwall, UK; South Carolina, USA; Georgia, USA and in Brazil. Hydraulic mining techniques are used at the Brazilian and Cornwall mines. Generally kaolin is dry mined, crushed and milled. This is the cheapest route from mining to processing. Particle size distributions are routinely expressed as an equivalent spherical diameter, esd. The highest (top) cut is typically at 75µm and refined clays range between 20µm-10µm. Kaolin can be used in an even finer size range using air-float or de-gritting methods. Most kaolin clays contain 50-99% kaolinite, some contain as little as 25% kaolinite. Mica, quartz and feldspar impurities make up most of the rest of kaolin.

2.3 Talcum

Talcum ($MgO.4SiO_2.H_2O$) is the softest mined mineral with a Mohs hardness value of 1. Like the calcium carbonates, talc exists prolifically around the world with particularly large deposits in Western Australia and France. Talc has been mined extensively using underground mining techniques, however in more recent decades, surface mining and open pit mining methods have become more widespread (Kennedy 1990). Talc particles tend to be within the 300-500nm size range though both fines and nano-talcum are receiving greater attention as reinforcing fillers for polymer (DePolo and Baird 2009). Talc is commonly used in paper making/coatings, as reinforcing in plastics and rubbers, in paints and in ceramics.

2.4 Titanium dioxide

Titanium dioxide (TiO_2) based composites normally comprise two of the three forms of TiO_2, these being anatase and rutile. Major TiO_2 mining operations are found in South Africa, Sierra Leone, Canada, Norway Australia and Ukraine. Open pit mines are typical for TiO_2 extraction and much of the mining is directed towards ore conversion to pure titanium. Both anatase and rutile have high energy surfaces and chemisorptions are common bonding mechanisms to these crystals (Andruszkiewicz 1990, Harris, 2004).

2.5 Table of physical properties of common mineral particles

Table 1 provides some rudimentary information on the physical characteristics of the mineral particulates described above.

3. Particle packing theory

The arrangement and distribution of particles will influence the properties of the composite and the structure of the pore space. Particle packing in nature is often found to be ordered

Particle	Shape	Density/ gcm^{-3}	Hardness (Mohs)
GCC*	Blocky, Cuboidal	2.7	3
Kaolin Clay	Platy, Hexagonal	2.6	2-2.5
PCC**	Acicular	2.7	3
Talcum	Platy	2.7	1
Anatase (TiO_2)	Acicular	3.82-3.97	5.5-6.0
Rutile (TiO_2)	Elongated to prismatic	4.23-5.5	6.5-7.0

*Ground Calcium Carbonate. **Precipitated Calcium Carbonate.
From (Besra et al 2000 , Broz et al 2006, Hauserman 1984, Holik 2006, Lam et al. 2009, Lerchenthal 1977, Meinhold 2010, Peters 1998)

Table 1. Physical properties of commonly used mineral particles

(Allen 1985). Particles used in composites are of different shapes, sizes, and surface chemistries. As a result, they interact differently with each other and with matrix materials. Particle packing theory has predominantly employed spheroids. Moreover, packing theory is generally restricted to pure particulate systems. Nevertheless, particles will tend to arrange within a composite according to the process arrangements and material properties/characteristics. Particles may pack more loosely than in compact packings but in a similar geometrical arrangement. Two classifications are oft used for random packings. These are loose and dense, and are in essence self explanatory (Cumberland and Crawford 1987). Dense packings are essentially those in which particles cannot easily move past each other, whereas loose packings are loose fit, easily moving particle packings.

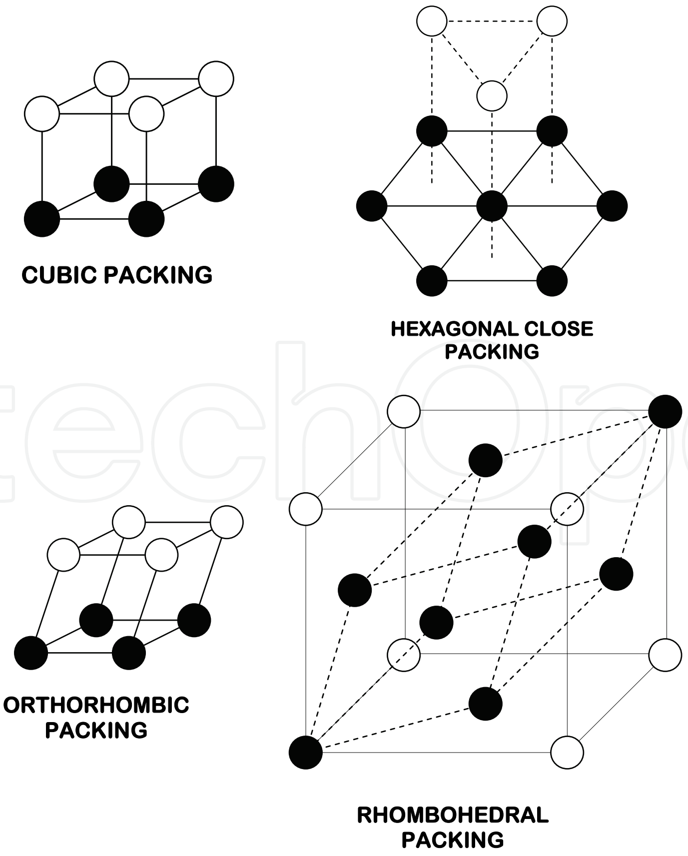

Fig. 1. Typical but idealised monodisperse packing arrangements

3.1 Idealised monodisperse sphere packings

A few idealised packing arrangements common to monodisperse spherical packings are shown in Figure 1. Particles in a packing occupying these positions and arrangements should be imagined as having larger particle diameters (almost touching) but are shown at distances in Figure 1 for diagrammatic clarity. Generally, the lower the matrix concentration, the closer the particles will pack and the more distinct the packing arrangement will be. Face centred cubic arrangements (not illustrated) are the tightest with a maximum packing fraction of 0.74. Hexagonal single layers are the tightest single layer arrangements. Porosity will arise when the matrix concentration is sufficiently low. Paper coatings are classic examples where the matrix concentration is so low that the pore fraction is often at around 30%. The highest possible coordination number for monodisperse spherical packings is 12. The coordination number can be defined as the integer sum of nearest neighbours, Figure 2. Nearest neighbours in powders and ceramics refer to those in a state of contact. In porous particle-polymer composites, the nearest particle neighbours can be considered as those that are conjoined by matrix material. In this sense, nearest neighbour definitions for such porous systems are simpler than those for filled system since in filled systems the particles may not actually be in contact.

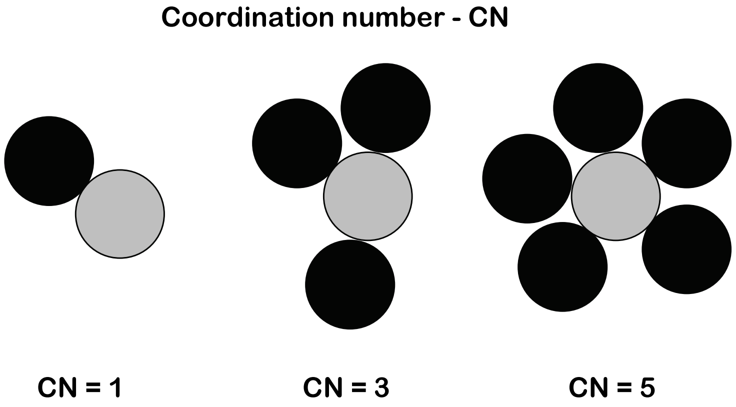

Fig. 2. Particle coordination numbers for particle systems are conceptually the same as for porous particulate-polymer composites. In both cases there must be contact between the particles, either directly or through a polymer matrix bridge

3.2 Polydisperse sphere packings

Polydisperse particle systems tend to have higher packing densities and average coordination numbers than monodisperse systems (Al-Raoush and Alsaleh 2007), Figure 3. A graph showing idealised packing density functions of monodisperse and binary packings is provided in Figure 4. In this figure, the binary packing refers to a two-particle polydisperse system. The secondary particle phase is considered an ‘inclusion’ therefore to an otherwise monodisperse system. One large particle in a polydisperse system may be surrounded by tens, hundreds or even thousands of contacting smaller particles, depending on the breadth of the particle size distribution. Volumes between larger particle contacts, depending on the size distribution, may act as particle-free volumes since particles can become trapped in regions close by, or the volumes are sufficiently small to prevent particle migration (Zok and Lang 1991). This is easiest to illustrate for binary particle systems, Figure 5. An idealised but typical graph comparing the coordination number frequencies for monodisperse and polydisperse systems is shown in Figure 6.

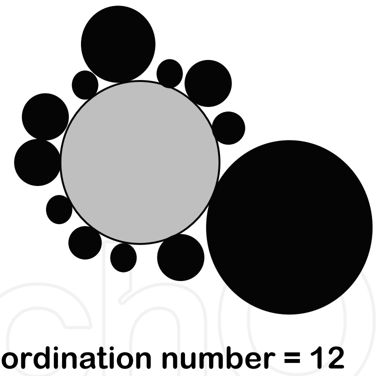

Fig. 3. Particle coordination numbers tend to be higher for polydisperse systems. The numerical value will depend on the breadth of the size distribution and the distribution of the particles and matrix material

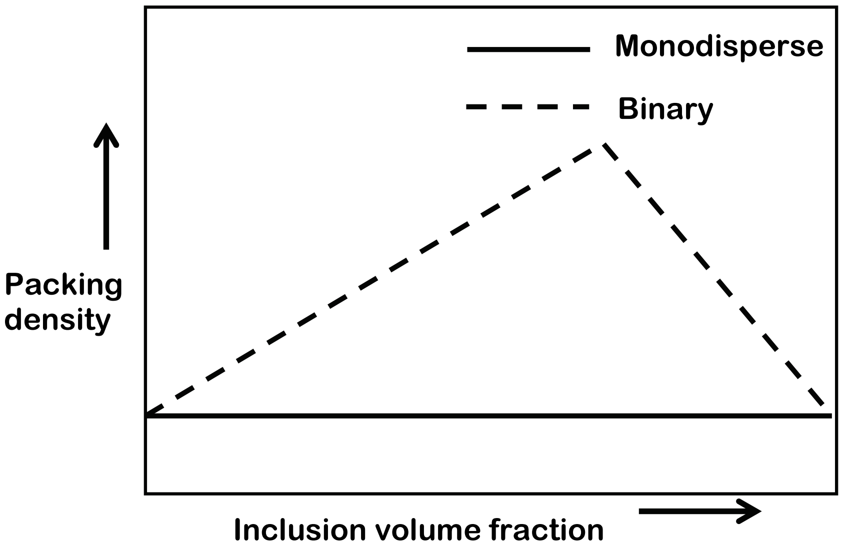

Fig. 4. Idealised packing density functions of monodisperse and binary packings

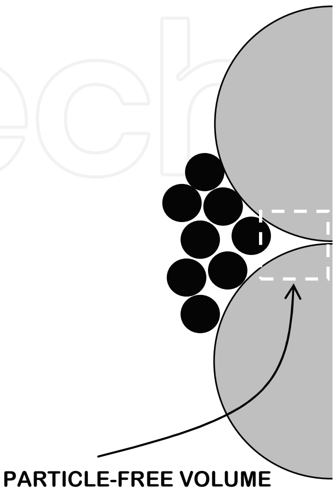

Fig. 5. Particle free volumes may arise through particle trapping as a function of the particle sizes

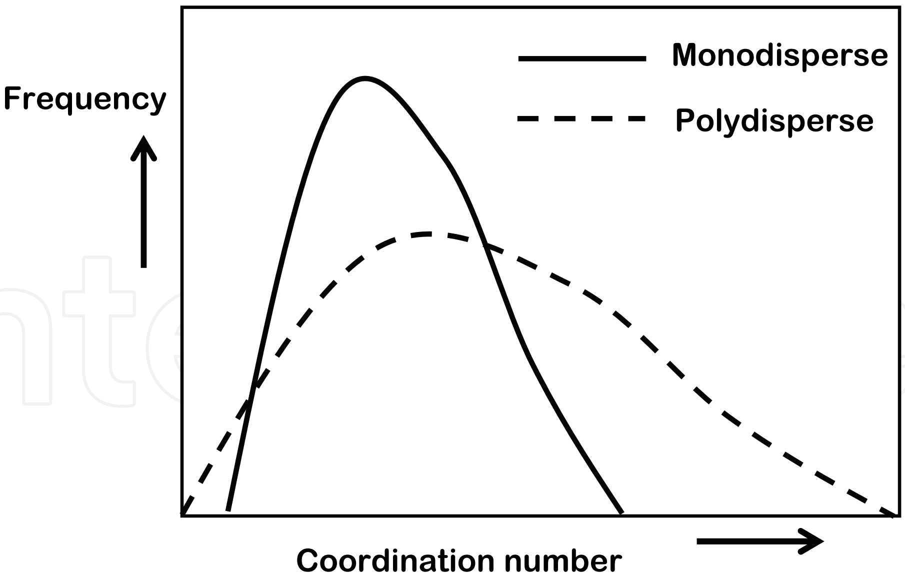

Fig. 6. Idealised but typical graph comparing the coordination number frequencies for monodisperse and polydisperse systems

3.3 Particle shapes

Many particle types used in porous composites are not spherical and cannot be justifiably approximated as such. Amongst the earlier classifications of particle shapes are those of Zingg (1935) who characterised four effectively cuboidal structures defined in Euclidean space according to a Cartesian coordinate system. The shape and orientation of particles distinctly impacts the properties of the composite material (Yamamoto and Matsuoka 1999, Abdul-Rashid and Akil 2008) and especially so with respect to the modes of failure and the fracture paths (Head and Rogers 1999). An ellipsoid for example may have the same sphericity as a sphere with surface protrusions, however, its influence on stress distributions and fracture, or indeed wetting and flow will differ considerably (Davis 1999). Typical particle geometries are shown in Figure 7. Of these particles, acicular particles exhibit the highest levels of microstructural heterogeneity (Alam et al. 2009) and platy particles laid relatively parallel pack very densely (Coulson 1949).

3.4 Computational packings

There have been numerous methods by which particles have been packed for computational and statistical analysis. For the most part computational packings have been made up of spheres or circles (Powell 1980, Scoppe 1990, Nolan 1992), often involving Monte Carlo methods; though, analytical shapes such as ellipsoids and spheroids have also been packed through discrete element methods (Ting et al., 1993; Lin and Ng, 1995). More recently, voxel digitisation has been used to successfully model arbitrary shaped random packings (Jia and Williams 2001, Byholm et al. 2004), which can subsequently be used for statistical, mass transfer and continuum mechanics simulations. The following are usually taken as minimal output requirements for computational packings (Davis 1999):

- Volume fractions of particles, polymer matrix and pores
- Dense and loose close packing fractions
- Coordination numbers
- Various distribution functions

- Particle and pore size distributions
- Distributions of various measures of surface curvature

In addition, the following should be deemed important further output parameters (Alam 2010):

- Anfractuosity (windiness of the solid state continuum)
- Tortuosity (windiness of the pore space continuum)
- Geometrical characteristics of the polymer matrix bridges
- Geometrical characteristics of the pore and neck space

The following section details briefly some of these parameters in respect of microstructure, influence and computation.

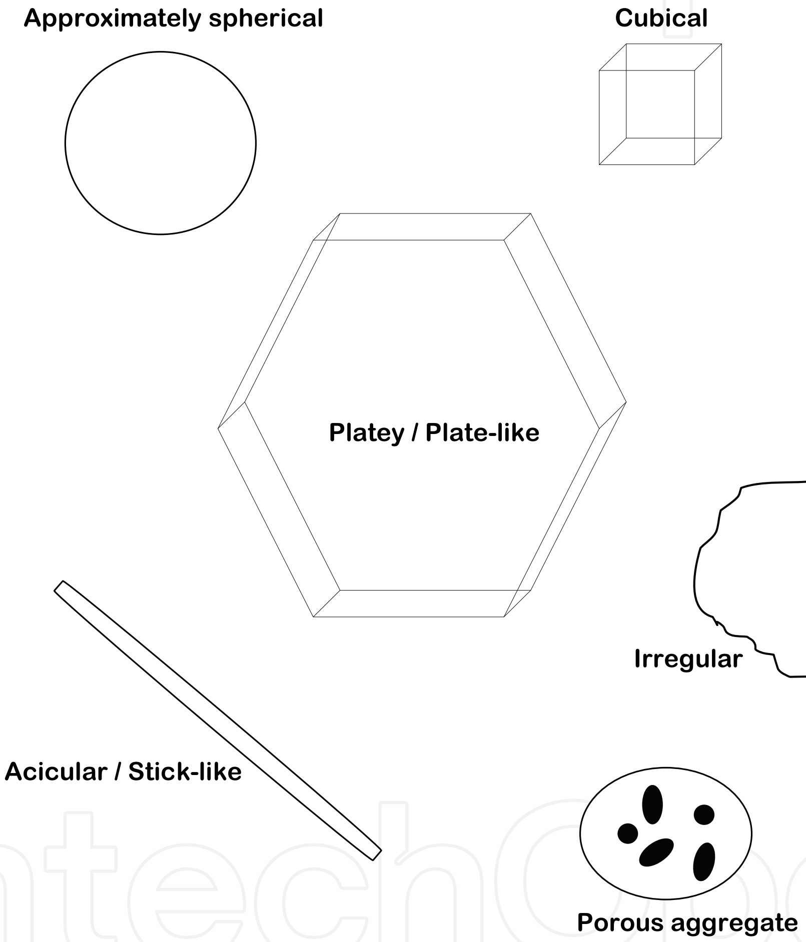

Fig. 7. Commonly applied approximations of particle geometries

4. Network connectivity in porous particle-polymer composites

There are essentially two ‘networks’ in any porous composite. These are the solid state network and the pore-neck network. This section outlines a few relevant issues pertaining to these networks.

4.1 The effects of pore space on microstructure and properties

Pore space dissociates the solidity of the composite. The levels of porosity, the pore size distribution and the pore-space connectivity may have both desirable and undesirable effects on the properties of particle-polymer composites. Pore size and porosity can to some extent be controlled however; very often pore-space characteristics are heterogeneous causing irregular properties throughout the body of material.

Porosity is a necessary characteristic for imbibition (mass transfer), breathability, heat insulation and opacity. It is for these reasons amongst others, that composites are often manufactured to have porosity. Provided the materials and the manufacturing methods are suitable, evenly sized and spaced pores can be incorporated into materials. Particle-polymer composites are different, since the particles tend to pack 'quasi-randomly' and packing arrangements are seldom regular. The most homogenous pore space and size distributions arise through using monodisperse particles. Varying the polymer content inevitably changes the packing arrangement and indeed, polymer clustering can occur in some cases, which further increases the heterogeneity of the porous microstructure.

The characterisation of pore space is as much philosophical as it is statistical. Should necks that are larger than pores be counted as necks or as pores for example? How should one define the beginning of a neck and the end of a pore? Can pores be reticulate and if so, at which geometry do they become porous networks? For reasons such as these, the simpler statistical methods of analysing pore space can be better, especially in view of comparative studies. Even small alterations in the throat geometry can have noticeable effects on the properties of mass transfer (Ridgeway et al. 2001) and the levels of statistical deviation (Yanuka et al. 1986). The simplest parameter to determine is usually the porosity itself, Equation 1.

$$p = 1 - V_s \tag{1}$$

Where p is porosity and V_s is the volume fraction of the solid state. There are various experimental methods and computational methods for determining this parameter. Amongst the more prominent experimental techniques are the direct methods (weighing comparison with volume), intrusion methods such as mercury porosimetry, water evaporation methods, optical methods (often coupled to image analysis/computational science) and gas expansion methods. Mercury porosimetry, optical methods and gas sorption methods can furthermore be used to calculate pore surface areas. Surface area values are useful in common permeability equations such as the Kozeny-Carman relation (Kozeny 1927, Carman 1937, Carman 1956).

4.2 Characterisation of pore space

Pore circularity is a statistical parameter that is of relevance to porous composites, especially since pore aspect ratios can significantly affect composite properties (for e.g. conductance, mechanical). Circularity, C, is calculated for 2-dimensional slices according to Equation 2.

$$C = 4\pi\left(A / \mathrm{P}^2\right) \tag{2}$$

Where A is the area of a pore and P is the pore perimeter. Circularity is essentially a measure of how close to a circle the pore is. The value lies between 0 and 1. A value of 1 indicates a perfect circle and as the value approaches 0, the pore is understood to have an increasing aspect ratio. Even if porosity is low, if a pore has a high aspect ratio and lies perpendicular to, for example, a loading direction, it will considerably reduce the load carrying capacity of the composite (Alam 2010).

Other useful statistical parameters include the Feret diameter and the pore coordination number. The Feret diameter is the longest diametral distance that can be found about the extents of a pore. The coordination number can itself be taken to be the number of pores that are connected to a single pore. Combining the coordination number as a product with the neck area/total pore area ratio yields a numerical value that indicates the level of differential permeability, and hence pore space disorder, within a composite structure (Alam 2009).

Tortuosity, τ, is a parameter which indicates the levels of delineation of a pore network through a composite. The simplest model of tortuosity (Epstein 1989) is calculated as,

$$\tau = {}^{h}\!/_{h_e} \tag{3}$$

where h is the shortest length through the measured section of composite and h_e is the shortest length through the pore network across the same stretch of material. Numerical values of 1 indicate that the pore network runs linearly through the composite. As this value increases, so too does the running distance through the pore network. The value of tortuosity for packed media is not constant. Increasing the size of particles for example, whilst retaining a constant porosity, may lead to reduced tortuosity (Petford and Koenders 2001). Decreasing the particle size also decreases tortuosity, provided the porosity also increases (Attia 2005). Typically, porosity increases as particle packings use finer particles (Cumberland and Crawford 1987). Models developed for spherical packings since the 1880's substantiate that tortuosity decreases non-linearly as a function of increasing porosity (Boudreau 1996). Dias et al. (2006) further consider the function to be that of an inverse power law, but primarily for granular and spherical packings within the range of porosity 0.4-0.5. Moreover, the non-linear trend between tortuosity and porosity is found to be true for both systematic and random packings (Kim and Chen 2006, Zalc et al. 2004, Moldrup et al. 2001). Non-spherical models, such as those of Koponen (1998) and Alam et al. (2006) suggest inverse linear proportionality between the two parameters. Ultimately, decreasing tortuosity is usually coupled to increasing porosity; however, changing the aspect ratio and shape of particulates will further alter this tendency. Moreover, complex pore space geometries can be the cause of unpredictable mass transfer behaviour and hence, values for tortuosity, due to the existence of cavities and 'nests' (Alam et al. 2006). Armatas (2006) has also suggested that tortuosity is more closely linked to the standard deviation of the pore size distribution and less so to the connectivity.

4.3 Anfractuosity of the solid state continuum

The structural stability of any porous composite will depend upon the network connectivity of the solid-state. A higher and more scattered volume of porosity tends to break up the solid state network continuum and increases anfractuosity; A. Anfractuosity can be taken to be the 'tortuosity' of the solid state. In that sense,

$$A = {}^{l}\!/_{l_e} \tag{4}$$

where l is the shortest length through the measured section of composite and l_e is the shortest length through the solid-state network across the same stretch of material. Higher values of anfractuosity result in lowered load carrying capabilities of the composite (linear load transfer being considered as 'ideal'). Conductance times are also increased as a result of greater anfractuosity in the solid-state. That coupled with porosity can sometimes give porous particle composites better insulating properties when compared with fully filled particle composites.

4.4 Polymer film formation

Mineral based particle composites with porosity will be bound by polymers. These polymers are normally added to slurry in fractions of weight. Properties worth considering before adding such polymers (e.g. styrene-butadiene latexes, acrylate-based latexes, starch-based polymers) include; polymer composition, colloidal properties (surface charges), rheological properties, mechanical properties, thermal and viscoelastic properties and surface energetics (Thümmes et al. 2009). When in contact with mineral particle surfaces, latex particles (often < 0.15μm) will spread. Subsequent film formation through further contact of latex particles (with each other) arises through a combination of compaction, cohesion and polymer chain inter-diffusion (coalescence). The formation of a defect free film will in turn depend on the temperature the latex particles coalesce under. The minimum film forming temperature (ASTM O 2354-68) should be reached for defect free film formation. Water must also evaporate for film formation to be complete. The procedure for drying such composites is governed to some extent by the properties of the composite components (such as solids content and burning temperatures), cross-linking characteristics and the dimensions of the material. Low solids content films dry much faster than high solids content films as there is less water to evaporate (Bierwagon 1979). Drying such composites too quickly can leave polymer films in a brittle state. Time should be allowed for the formation of polymer chain entanglements, which give rise to greater ductility within the cohered film (Gauthier et al. 1996). Film formation can be summarised accordingly (Steward et al. 2000):

- Evaporation, particle concentration and ordering
- Particle deformations, compaction and cohesion
- Polymer chain diffusion across particle boundaries

Mineral particle surfaces, following surface treatments with dispersing agents or surfactants, may comprise carboxylate groups. Such groups encourage interfacial cross linking not only between mineral (or dispersant) and polymer matrix, but also between latex particles. The formation of hydrogen bonds or ionic dipolar interactions eventuates in improved viscoelastic cohesive strengths of latex films and adhesive strengths at interfaces (Richard and Maquet 1992).

5. Polymer structure variations in porous particle-polymer composites

The presence of particulates may alter the structure and properties of the polymeric matrix within which it is held. Interfacial pinning for example, is an immobilisation of polymer chains at particle interfaces. This is true for interfaces that are purely particle-polymer as well as in cases where a layer of polar molecules (such as dispersants/surfactants) encapsulates the particle.

5.1 Polymer chain pinning

Polymer chain pinning can be considered as analogous to adhesion. Since many properties of composites rely on strong intermolecular forces of attraction between polymer and particle, pinning is to an extent, a desired characteristic (Lepoutre 1994, Nielson 1966). Pinned polymer molecules are unable to move at one end and as a result have different characteristics to bulk polymer molecules. The thickness of this immobilised layer is difficult to predict or calculate. This immobilised layer is likely to be thinner in composites containing porosity because polymer molecules have more freedom to relax and orient to a lower energy state when there is less ambient resistance. Evidence and theory underlying the effects of polymer pinning on the dynamic properties can be found in Touaiti et al. (2010). The immobilised layer thickness in most particulate composites is generally in the range 1-50nm, (Rothan 2003) and varies as a function of particle size (Tan & McHugh 1996). The presence of particulates and the pinning of polymer molecules to particle interfaces may also restrict movement of polymer molecules as effectively, space limitations exist. Polymer molecules will moreover, orient according to lowest energy state principles and the presence of particles alongside pinning effects will guide somewhat the state of molecular orientation. For this reason, particles can act as nucleation sites and polymer crystallinity and orientation becomes a function of particle presence (Cho et al. 2002). Smaller particles (especially of the nano-scale) are highly effective as nucleating sites and can easily disrupt existing crystal structures (Bhimaraj et al. 2007, Yuan et al. 2006). Polymer chain pinning affects properties such as fracture strain, stiffness, and hardness (Akinci 2010). These are all in turn related to changes in activation energies for fracture, and energy that can be stored by pinned chains as compared to free moving chains. Interparticulate distances and particle surface areas will furthermore hinder to a greater or lesser degree, the polymer chain mobility. Smaller interparticulate distances and higher surface areas restrict mobility more effectively (Traina 2008). Porosity within the composite promotes 'free movement' of chains at free surfaces and reverses somewhat, the effects of pinning on the mechanical and viscoelastic properties of the composite (Mansfield & Theodorous 1991, Baschnagel & Binder 1995). Pores can thus act as 'relaxation' zones, which allow for increased free surface areas of the inter-pore polymer confinements.

5.2 Changes in the molecular weight through degradation and cross linking

Polymeric material degrades in the presence of particles thus reducing the molecular weight. This degradation may be onset by mechanical, thermal or chemical means. Degradation is often exacerbated in process operations such as moulding, extrusion, compounding and through the application of heat and pressure. Chemical interactions at the interface may deactivate stabilisers and antioxidants in the polymer, or, may simply be chemical species that degrade polymers such as surface-present enzymes in biodegradable composites (Cooper et al. 1995). Thermo-mechanical degradation that can occur during processes such as extrusion, is a result of highly localised interfacial frictions resulting in micro-scale mechanisms of erosion. Degradations, whether thermal, mechanical or chemically instigated, have a quite direct impact on the properties of the final composite (Traina 2008, Choi et al. 2005). However, the contribution to the overall properties through the particles themselves, result in mechanical enhancement even though there may be considerable evidence of polymer degradation (DePolo 2009). Mechanical work is probably the greatest contributing factor to degradation and the effects of particulates on polymer degradation is most pronounced when polymer viscosities are high. It should be noted that particle degradation also occurs (Fisa et al. 1984) during the processing stage with polymer. The level of mechanical degradation to the particle will however, be highly dependent on the properties and characteristics of the particle relative to the process conditions and the properties of the polymer. The molecular weight and crosslinking characteristics of the polymer can also change during curing. The curing process determines the eventual molecular structural details of free-radical cured polymers, which in turn influence the polymer properties. Particles create variations in the curing process and thence the final properties of the polymer. These variations include; (a) lowering of the overall exotherm thus reducing the cure temperature and kinetics of curing and (b) particle surface chemistry altering the stability of the polymer at the interfaces (Rothan 2003).

5.3 Additives – for modification to surfaces and to polymer structures

Additives such as dispersants, surfactants, coupling agents, plasticisers and stabilisers will often adsorb more readily to a particulate surface than a polymer matrix material. This creates polymeric regions close to the particle interfaces with a lower molecular weight than the virgin polymer matrix. Without these additives, process and manufacture of porous particle-polymer composites with sufficient homogeneity is almost impossible (most notably due to particle agglomeration). In the cases of typical carbonate-latex coatings, dispersing agents used bind preferentially to calcite surfaces and the latex is effectively adhered to the surface of the dispersing agent. In such a case, there are essentially two interfaces in place of one, the calcite-dispersant interface, and the dispersant-latex interface. In some cases, surfactant adhesion to particulate surfaces can in fact improve the overall strength of the composite, provided the polymer-surfactant bond strength is superior to that of the polymer with the particle. A short list of common polymer additives from Stevens (1993) is provided in Table 2.

Additive	*Purpose*
Additives for the modification of surface properties	
Antistatic agents	Prevention of build up of static charges
Coupling agents	Interfacial bonding agents (for better bonding)
Release agents	Prevention of particulate sticking
Additives for the modification of chemical properties	
Antioxidants	Prevention of oxidative degradation
Additives for aesthetic pleasure	
Colouring agents	Optical/colour properties
Nucleating agents	Optical properties
Additives for process control	
Cross linking agents	In the curing process
Emulsifiers	Stabilisation of polymer emulsions
Heat stabilisers	Prevention of thermal degradation
Plasticisers	Lower the melt viscosity
Release agents	Prevention of particulate sticking
Thickeners	Increase the viscosity of the polymer

Table 2. List of common additives

6. Composite models for porous particulate materials

The most common engineering models for composites cannot be satisfactorily applied to porous particle-polymer composites. Various models suggested for porous two-phase particulate ceramics provide a good starting block for understanding how porosity affects particulate composites. The simplest of these models is that occupied by Voigt bounds such that the elastic modulus of the porous material, *E*, is inversely proportional to porosity, φ. In this model, E_c is the composite elastic modulus (assuming isotropy and no porosity).

$$E = E_c\left(1-\phi\right) \tag{5}$$

This model, though simple, has drawbacks in that it does not usually yield sound predictions for porous composites. Generally, non-linear models are found to be more accurate. Phani et al. (1988), Maitra and Phani (1994) and Wagh et al. (1993) have suggested the use of the following relationship, Equation 6, which is essentially an exponential modification of the linear expression (Equation 5). In this equation, *a* and *b* are constants, or, fitting parameters.

$$E = E_c\left(1-a\phi\right)^b \tag{6}$$

For the most part models used to predict the non-linear elastic modulus characteristics of multi-phase materials use such fitting parameters. This is often expressed by including a numerical exponent such as is shown in Equation 7, (Brown et al. 1964) and refer to Phani et al. (1988), Maitra and Phani (1994) and Wagh et al. (1993). The elastic modulus can also be expressed as being a product of the composite elastic modulus and e^m, Equations 8 and 9, (Rice 1977, Knudsen 1959).

$$E = E_c\left(1-a\phi^{2/3}\right) \tag{7}$$

$$E = E_c e^{-a\varphi} \text{ for } \phi \le 0.5 \tag{8}$$

$$E = E_c e^{-a(1-\varphi)} \text{ for } \phi \ge 0.5 \tag{9}$$

Further modified non-linear expressions for the elastic modulus of multiphase porous composites include fitting parameters that are a function of the pore aspect ratios, A_r, Equations 10 and 11 (Janowski and Rossi 1967, Boccaccini et al. 1993).

$$\begin{gathered} E = E_c\left(1-a\phi\right) \text{ for } \phi \le 0.5 \\ a = f\left(A_r\right) \end{gathered} \tag{10}$$

$$\begin{gathered} E = E_c\left(1-\phi^{2/3}\right)^{1.21a} \text{ for } \phi \le 0.5 \\ a = f\left(A_r\right) \end{gathered} \tag{11}$$

Equations of the generic form (Hashin 1962, Ramakrishnan and Arunachalam 1993),

$$E = E_c \frac{(1-\phi)^n}{1+k\phi} \tag{12}$$

include an additional parameter k that incorporates Poisson's ratio effects of the solid state into the model. These models have for the most part, been taken into consideration for two-phase (particle-air) composites. Models concerned with the prediction of three-phase (air-particle-polymer) composites are generally derivatives of the classical mixture's models (Voigt 1889, Reuss 1929, Halpin-Tsai 1969). These models shown in Equations 13, 14 and 15 respectively, are such that the volume fractions, F, of matrix, $_m$, and particle, $_p$, must be fractions of the composite including the extra air that exists through porosity.

$$E = E_p F_p + E_m F_m \tag{13}$$

$$E = \left(\frac{F_p}{E_p} + \frac{\left(1-F_p\right)}{E_m} \right)^{-1} \tag{14}$$

$$E = \frac{E_m\left(1+\xi\eta F_p\right)}{\left(1-\eta F_p\right)} \tag{15}$$

where $\eta = \frac{\left(E_p / E_m\right)-1}{\left(E_p / E_m\right)+\xi}$ and $\xi = 1$

Needless to say, none of the classical models have shown they can be successfully used to predict the elastic modulus of porous particle-polymer composites. The Reuss and Halpin-Tsai models being "lower boundary" definitions usually yield the closest predictions, though these are still usually far out (Xu 2006). Alternative models specifically for fully-filled particle-polymer systems have been suggested by Eilers (1941), Brinkman (1952), Nielsen (1969), Narkis (1976) and Thomas and Muthukumar (1991). These being contemporary non-porous models, will not be reviewed herein.

McAdam (1951) modified the Reuss model to include a linearly proportional reduction of the elastic modulus as a function of increasing porosity, Equation 16.

$$E = \left(\frac{F_p}{E_p} + \frac{\left(1-F_p\right)}{E_m} \right)^{-1} \cdot (1-\phi) \tag{16}$$

Bert (1985), preferred to modify the Halpin-Tsai model with a slightly more complex reduction term. The Bert model includes a composite term that takes into consideration the relative pore space and the pore shape. This model, Equation 17, assumes K_0 = 2 for spherical pores.

$$E = \frac{E_m\left(1+\xi\eta F_p\right)}{\left(1-\eta F_p\right)} \cdot \left(1 - \frac{\phi}{\left(1-F_p\right)} \right)^{K_0\left(1-F_p\right)} \tag{17}$$

A comprehensive model suggested by Alam (2010), Equation 18, factors into the mixtures' model of Voigt; an 'effective' binder fraction, a stress transfer, s_t, aspect ratio, L_p/d_p, product for the particles, an anfractuosity parameter, A, and an effective pore width ratio, $w_{p,\max}\,w^{-1}$. When compared with the Voigt, Reuss, Bert and McAdams models, against both experimental and simulation results, this model was found to yield the most accurate predictions.

$$E = \left(E_p F_p \left(\frac{\overline{L_p}}{d_p} \cdot \frac{1}{s_t} \right) + E_m F_{c,eff} \right) \cdot \frac{1}{\overline{A}} \cdot \left(1 - \frac{w_{p,\max}}{w} \right) \tag{18}$$

If there are no pores then $A = 1$ and $w_{p,\max} = 0$.

7. Surface science

The utility of any composite will be influenced by the strength and intimacy of the bond between the components. Many factors affect the bonding between components in a composite. These include at least wetting, roughness and the mechanisms of adhesion, all of which are interconnected.

7.1 Adsorption and wetting

The spreading of liquid across a solid surface and its ability to maintain contact is wetting. Wetting is a function of the intermolecular forces of attraction at the contacting surfaces. The extent of wetting is determined by the balance between adhesive (interfacial forces) and cohesive forces of attraction within the body of fluid. Higher adhesive forces encourage spreading while higher cohesive forces make the body of liquid curl into a ball. The droplet contact angle is the angle at which three phases meet (solid, liquid and gas). The droplet contact angle is an indicator of the level of wetting, and hence the relative strengths of the adhesive and cohesive interactions. Very low contact angles indicates high wetting favourability while very low contact angles mean the liquid does not wet the solid surface very well. Figure 8 shows examples of non-wetting, wetting and high (near-perfect) wetting surfaces.

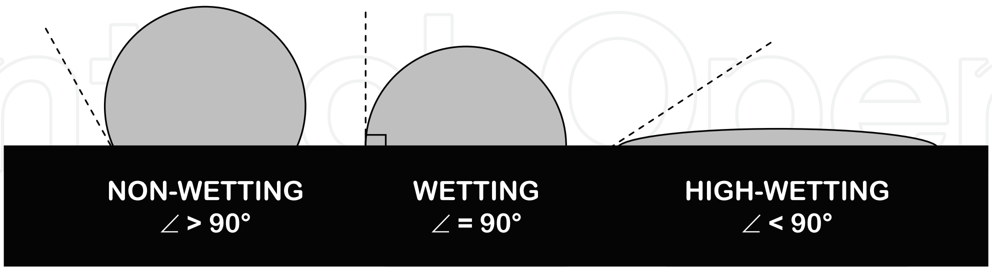

Fig. 8. Examples of non-wetting, wetting and high-wetting

Other factors that influence wetting include the liquid viscosity, the surface roughness and ambient pressures. The 'equilibrium' state of a droplet on a surface, Figure 9, is represented by Young's equation, Equation 19,

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos\theta \tag{19}$$

where γ is the surface energy between two phases.

Interactions at the interface of polymer and particle govern the spreading characteristics and ultimately the strength of the adhesive bond between the two. Ingress of polymer matrix into particle bodies is possible when the particles have holes, defects or micro-/meso-pores. Ingress such as this increases the number of interfacial interactions and mechanical interlocking, and consequently improves adhesion (Van Meer et al. 2009). Polymer droplet spreading/ingress behaviour is however, further complicated by factors such as the topography of the particle surface and external influences that may alter the flow and properties of the polymer matrix (pressure, temperature). The properties of the polymer (e.g. viscosity) relative to the topography and surface energies are paramount in wetting.

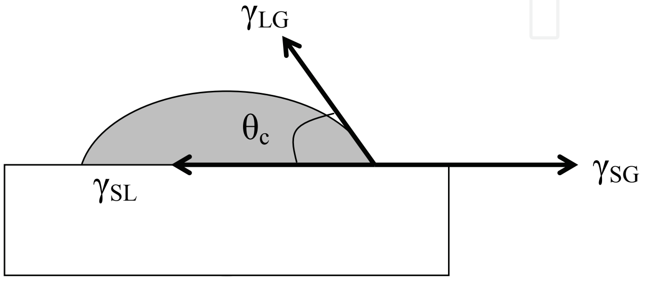

Fig. 9. The equilibrium state of a droplet is represented by Young's equation, Equation 19

7.2 Roughness

Packham (2003) justifies that the forces of attraction between two surfaces may be enhanced by increasing roughness, provided that the topographical profile does not reduce the total area of contact. A commonly employed roughness parameter is the R_a roughness. This is effectively a measure of the mean protruding to intruding height differentials about the average height. It is expressed as,

$$R_a = \frac{1}{L}\int_0^L |z(x)|\,\mathrm{d}x \tag{20}$$

where $z(x)$ is the local height of the surface and L is the sample length. R_a roughness is a deficient parameter in that it only measures the height differentials about the topography and high scatter that is often coupled to the use of the R_a roughness comes down to the lack of topographical detail defined within this parameter (Range and Feuillebois 1998).

Wenzel roughness (Wenzel 1936) is another oft used approximation for roughness. The Wenzel roughness, r_w, is defined as,

$$r_w = \frac{A_T}{A} \tag{21}$$

where A is the nominal surface area and A_T is the true area of cross section. This parameter works adequately for low levels of roughness (Packham 2003) and is quite easy to modify (McHale and Newton 2002) since it is an inherently simple model. Alam (2007) suggested the Wenzel roughness be used as part of a more explicatory topographical definition of roughness, φ, (Equation 22) which when compared against Wenzel roughness, was found to generate less scatter in droplet spreading simulations. In this equation, A_r is a ratio of mean protuberance height to a square root of the protuberance cross section, and F is a normalised protuberance frequency term. There are numerous mathematical definitions of roughness (Stout et al. 1994) which have been compared in Bernardin and Mudawar (1996).

$$\varphi = \frac{r_w \times A_r}{\mathrm{e}^F} \tag{22}$$

Roughness coupled to increased or decreased surface energies are ways by which coupled interactions can be amplified or diminished (Miwa et al 2000, Zhang et al. 2006, McHale et al. 2004). Particles exhibit roughness and particle shape specifications based on fractals have been suggested (Kaye 1989). On solid materials free of porosity, such as ceramic crystallite particles, a Tanner's law tendency is typically accepted as descriptive of droplet spreading behaviour and has been experimentally verified (Landry and Eustathopoulos 1996). Accordingly, Tanners law is $D_n \sim t^n$ where D_n is the diameter of spread, t is time and n is a constant. This law has also been found to hold true on porous solids (Holman et al. 2002) irrespective of the fluid imbibition that may take place within the first moments of contact, and indeed, irrespective of 'pinning' to the droplet protuberances (Raiskinmäki et al. 2000). Flow into porous media, and hence particle, is taken to be capillary driven (Alleborn and Raszillier 2004) however interfacial pressure pulsations (Toivakka 2003) may also give rise to increased volume ingress of polymer into particulates.

7.3 Surface energies

A final point that shall be made with regard to wetting is that of high and low energy surfaces. Metals and ceramics have what is said to be high energy surfaces. These materials are metallically or covalently bonded (primary bonds) and high levels of energy are required to break such bonds. Low energy surfaces are usually found on materials such as polymers, where the body of material is held together by weak secondary bonds (Van der Waals). The lower the value of γ_{LG} and θ, the more wetting a liquid is likely to be.

7.4 Mechanisms of adhesion

There are a number of interdependent mechanisms that govern the strength of bonding between individual composite materials.

Mechanical interlocking is one such mechanism. This is essentially a topography based effect, with specific topographical profiles yielding superior interlocking characteristics. Surface preparation/treatment is nonetheless important in its own right and the effectiveness of mechanical interlocking will to a great extent; depend upon the ease of permeation into valleys, holes and general topographical irregularities. This is a function of both the liquid/matrix material and the shape of the protuberances. A mechanically roughened substrate has the benefit of increasing the surface area available for adhesion, however if there is insufficient intimate contact, adhesion may in fact be lowered. Additionally, the shapes of certain surface irregularities may in fact increase the local stress concentrations when the composite, or the interface, is in any way strained. There are many possible surface shapes and configurations for surface irregularities. Biomimetic 'mushroom shaped' protuberances show great potential in enhancing the strength of adhesion. Porous materials such as wood, paper and certain large-pore ceramics have tortuous pore networks. Permeation and setting of adhesive/matrix into these networks will heighten the effects of mechanical interlocking. **Molecular entanglements** of polymer molecules at interfaces also have the effect of improving the strength of interlocking. **Secondary force interactions** are perhaps the dominating interactions within *adsorption theory* of adhesion. The adsorption theory proposes that materials will adhere so long as there is sufficiently intimate contact between them for intermolecular forces of attraction to develop. Generally Van der Waals bonds dominate interface interactions between materials, however hydrogen bonds can also develop. **Electrostatic attraction** is a secondary bonding mechanism where oppositely charged surfaces interact. This can be dipole-dipole interaction, or, cationic-anionic couplings. **Chemical bonding** (primary bonding) may also occur across the interface; however '*chemisorptions*' as they are so called, are not as common and normally require special techniques during the process of manufacture. Bond energies for primary bonds can range from 60-1100 kJ/mol and 0.08-40kJ/mol for secondary bonds. **Polymer diffusion** and migration between contacting interfaces (*diffusion theory*) are means by which polymers adhere to each other (autohesion). This theory deems essential, high molecular chain mobility at interfaces for diffusion to take place alongside similar levels of solubility. Generally, long chain segments maintain position in the host polymer and chain ends will diffuse into adjacent polymeric material. The consequence is that the short segment of chain effectively 'anchors' itself into adjacent polymer and if this process repeats sufficiently, polymer-polymer adhesion occurs. **Molecular entanglements** may form when chain segments are sufficiently mobile. **Interphase regions** are regions of contacting materials that have combined local composite properties of both materials. Familiar day-to-day materials with interphase regions include "adhesive-wood" in jointed wood composites, "binder-paper" in coated paper composites and polymer-polymer in joined polymers (joined through polymer chain diffusion). The extent of influence such interphase regions will have on the composite properties will depend on a number of factors including but not limited to; depth of penetration relative to depth of composite, properties of penetrated/adsorbed material relative to substrate, intimacy of bonding between materials within the interphase, and the topographical profile. There are various tests that are used to determine the **strength of bonding** between two materials. The most ideal situation of bonding is one where failure occurs within one of the materials as opposed to at the interface between them. This means that the bond strength is not the limiting factor for strength, and that the materials are being used to their fullest potential. Typical bond strength measurements are done using fibre pull out tests, fibre push out tests, peel tests and shear tests.

8. Environmental footprint of mineral particle-polymer composites

Considerable effort and money is expended on issues related to, and for the improvement of, the environment. Materials, excavation, manufacturing routes and ultimately waste management are all matters that should be considered when designing composites. Since focus in this chapter is essentially on mineral pigment-latex composites, it is appropriate to begin with a small section on raw sources of materials.

8.1 Raw sources of mineral particles and conversion

Mining is currently the dominant method for excavating mineral ores. Different mining approaches to excavation have been mentioned in sections 2.1 to 2.4. Mining from start to finish is a 5 stage process. These stages in chronological order are; prospecting, area exploration, mine construction, mining and dismantling of mines with environmental restoration. The main types of mining used for excavating minerals/mineral ores are quarrying, open pit mining, surface mining and underground mining. The main negative effects mining has on the environment can be summarised as follows:

- **Air pollution:** dust particles through explosions, release of sulphur dioxide, release of greenhouse gases
- **Damage to ecosystems:** destruction of animal habitat, leeching of chemicals foreign to the host environment
- **High energy consumption:** mine construction, maintenance of mine safety and temperature, use of machinery, transportation
- **Land pollution:** felling of forests to create mines, generation of large underground fault lines, exacerbation of land erosion
- **Water pollution:** sulphides released acidify local water supplies, aquatic life affected

Mining is however indispensible if the intention is to maintain a high standard of living. The mining industry creates jobs and generates money locally, nationally and globally. The ecological effects are usually short term and environmental rehabilitation is a legal requirement in most countries. The extent to rehabilitation does nevertheless vary. Mining has also become far safer, with a fifteen fold drop in mortalities and a four fold drop in injuries since the late 1930's. Mine debris can moreover be disposed of inside the mine, making rehabilitation easier.

There are several energy-intensive operations in converting the mineral ore to mineral particles readied for use. For kaolin particles, these include; high pressure water pumps, clay mica thickening tanks, clay fractionation or centrifugation and the separation of clay particles based on size.

8.2 Raw source and conversion of polymers used in particle-polymer composites

The origin of many polymers used in composite materials is crude oil. Similarly to mineral ores, crude oil is a finite resource. The numerous environmental issues brought on by the oil exploration and production industries include habitat protection and biodiversity, air emissions, marine and fresh water discharge, soil and groundwater contamination and oil spills (Visser and Larderel 1997). The route to styrene butadiene latex is process-intensive. Naptha is one of the many products that is output from heating crude oil. Naptha then needs to be reformed for benzene, which is used to produce ethylbenzene and subsequently styrene. Styrene, through the procedure of alkylation and combination with acrylonitrile is transformed to styrene butadiene latex polymer. Production of latex generates both recycle oil and white water. These are considered hazardous wastes that are capable of contaminating ground water supplies, rivers and lakes. Moreover, short-term inhalation of styrene is a respiratory hazard, irritates eyes and causes gastro-intestinal problems.

8.3 Disposal and recycling

Ordinarily incineration is the preferred method of disposal since the particles are not always deemed worth retrieving and the volumes of polymer in the systems are normally very low. If there is a concerted effort to actually recycle the polymeric phase of composites, this is then possible by acid treatment. Acid treatment has the added benefit of removing dispersing agents from particle surfaces. The use of biodegradable polymers is one possible means by which the environmental footprint can be decreased. These can be produced from both renewable sources (gluten, starches, corn based thermoset polyester, soy protein resin), and from crude oil sources (polybutylene succinate (PBS), polycaprolactone (PCL), polyvinyl alcohol (PAV/PVOH)). Many biodegradable polymers undergo photobiodegradation, which is onset by UV light. Others degrade through mineralisation. This is effectively, the use of specialised bacteria to break down polymer to lower molecular weight species followed by a conversion to CO_2 and H_2O. Prodegradants such as catalytic metal compounds based on iron, cobalt and manganese may also be used to trigger and/or accelerate polymer degradation. Biolatexes are biodegradable polymers that can be derived from both petroleum (Figliolino and Rosso 2009) or natural sources such as starches (Bloembergen et al. 2010). These polymers are considered carbon neutral (Figliolino and Rosso 2009, Bloembergen et al. 2008) and are often also biodegradable. Carbon neutral polymers take generally 10^4 less time to convert carbon within their natural cycle of conversion than fossil carbon, thus remaining for considerably shorter times in the atmosphere.

9. Conclusions

There are a great many considerations in designing, manufacturing and engineering particulate-polymer composites with porosity. Accurately predicting strength and stiffness, and designing to improve durability is no trivial task. Models are continually being updated to reflect new theories on the more prominent and influential features of microstructure, in relation to properties. Mass transport issues also require manufacturing routes through which pore microstructures can be controlled and perhaps even manipulated. Surfaces may be designed to have improved brightness, opacity and wetting control. These issues again, rely on the ability to control the geometrical and chemical makeup of such composites. Porosity is a desired property when weight, optical properties and flux properties are of primary concern. The presence of pores does however negatively affect the mechanical properties and durability of the composite. Moreover, the extractions of raw materials, their processing and ultimately composite manufacture are all energy intensive ecologically damaging and environmentally polluting stages prior to use and disposal of the final product. There are a few ways by which the environmental footprint left over the life-cycle of these composites could be minimised, though to implement these would require that damages to the economics and finances at each stage are negligible.

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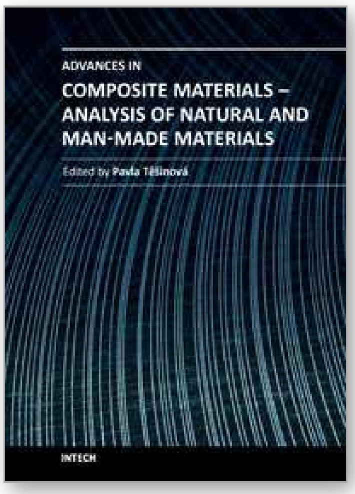

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Composites are made up of constituent materials with high engineering potential. This potential is wide as wide is the variation of materials and structure constructions when new updates are invented every day. Technological advances in composite field are included in the equipment surrounding us daily; our lives are becoming safer, hand in hand with economical and ecological advantages. This book collects original studies concerning composite materials, their properties and testing from various points of view. Chapters are divided into groups according to their main aim. Material properties are described in innovative way either for standard components as glass, epoxy, carbon, etc. or biomaterials and natural sources materials as ramie, bone, wood, etc. Manufacturing processes are represented by moulding methods; lamination process includes monitoring during process. Innovative testing procedures are described in electrochemistry, pulse velocity, fracture toughness in macro-micro mechanical behaviour and more.

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