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Surface and Interface Phenomenon in Polymers

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SURFACE AND INTERFACE PHENOMENON IN POLYMERS

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Short Course 2008

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SURFACE AND INTERFACE PHENOMENON IN POLYMERS

OUTLINE:

- Introduction : Scope of the short course
- Surphase phenomena
- Adhesion phenomena
- Polymer-polymer adhesion
- Polymer surface modification
- Polymer surface identification
- Polymer adhesive materials
- Nanomaterials
- Optimal (effective) interface/interphase
- Conclusion
- Literature

Introduction

- **Surface and adhesion phenomena:**
- **Basic concepts for understanding**: Processes at the polymer boundary layers; Definitions of interface/interphase; Interface polymer layers; Surface modifications and identifications; Polymer materials where the interface plays a crucial role in determining the properties: Adhesives, Polymer composites, Nanosystems.

- **Scope of the short course:**
- **Overview on the surface and adhesion phenomena at interfaces in polymer systems as a base for surface and interface engineering and creating the new multiphase polymer nanomaterials**.

Surface phenomena

Surface nature of polymers

- **The behaviour of polymers at interfaces** is of fundamental importance in a **wide range of technologies and applications :**
- **Industrial processes** imply **surface active components** such as catalysts, colloids, surfactants, adhesives, coatings.
- **Adhesion, lubrication**, **stabilization,** controlled **flocculation** of colloidal dispersions, **biological macromolecules** function at **natural interfaces** such as cell membranes etc.
- **Adhesive and coating properties** (e.g. heat sealing, reinforcing etc.);
- **Polymer processing and machinery handling** (e.g. friction, self-adhesion, welding of two peaces of polymer by thermal or solvent bonding as a common example of strength development by polymer-polymer interface).
- **Development of various products** are based on the unique properties of interfaces (photographic films, adhesives, membranes, composites etc.).

Surface nature of polymers, *cont.*

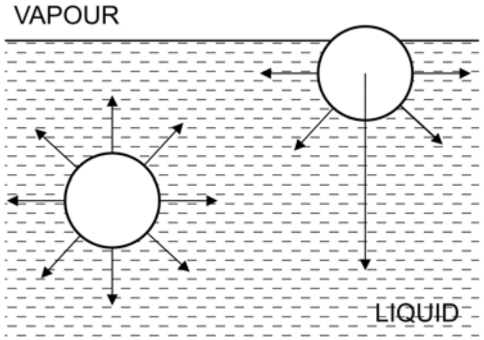
- **Different nature of polymer surface than in the bulk:**

- **Different molecular weight** (segregation of low molecular weight ‘tail’ polymer);
- **Deliberated additives** (antioxidants, emulsifier, fire retardant, stabilizers, agents for lowering surface friction, aid processing etc.);
- **Segregated lower energy component** (e.g. in segmented copolymers, lubricating oils, greasiness, mould release agent etc.);
- **Migration of additives across the interfaces** through contact with another surfaces (e.g. filler and pigments, surface coating etc.).

Surface phenomena, *cont.*

Surface energy

- **<u>The resultant forces on molecules</u> inside and at the surface** are different:



- There is an **excess energy in the surface** (of a solid or liquid) and the correlation between the **magnitude of surface energy** and the **bonds strength** that have to be broken (dispersion, hydrogen, metallic etc.) e.g. differences in surface energy of a paraffin (22 mJm^{-2}), water (72 mJm^{-2}) and mercury (465 mJm^{-2}).
- The energy necessary to break these bonds is the **surface energy**.

Surface phenomena, *cont.*

Surface energy, *cont.*

- **Surface energy, γ,** should be regarded as the sum of the energy required to break the all bonds that have to be broken:
- **Fowkes** suggested :

$$\gamma = \gamma^{d} + \gamma^{p} + \gamma^{h} + \ldots$$

where superscripts refer to dispersion forces (d), polar forces (p), hydrogen bonding (h) and others.

- **Surface** is always a part of **an interface** (even if another phase is vacuum).
- The term '**surface energy**' applies strictly for the substance **in contact with vacuum** - in **practice** the surface is in contact with air or vapour.

Surface phenomena, *cont.*

Surface tension and surface energy

- **Surface tension** is a concept allied with **surface energy:**

Molecules and/or **atoms** at the **surface**
are due to the attractions from the bulk) in the condition of

higher surface tension	and/or	**higher surface energy**
as a result of		as a result of
intermolecular forces		**intermolecular distances**
that tend to separate		for that is necessary the additional
the number of **molecules**		work for keeping **molecules**

at the surface

Surface phenomena, *cont.*

Correlation between surface tension and surface energy

- **The basic:**

- **Thermodynamic concept** of **surface tension**, γ, as the partial differential of the Gibbs free energy (G) of the system with the respect to the area *(A),* at the constant temperature (T) and pressure (P):

$$\gamma = \left(\frac{\partial G}{\partial A} \right)_{\mathrm{TP}}$$

- **Thermodynamic consideration** of **surface energy :** the Gibbs surface free energy (G^{S}) as the excess of free energy associated with the surface (A), between the total free energy (G) of the system and the one in the bulk (G^{B}):

$$G^{\mathrm{S}} = \frac{G - G^{\mathrm{B}}}{A}$$

Correlation between surface tension and surface energy, *cont.*

- The **difference in attraction forces** between molecules in the bulk and at the surface is the reason of the existence the **surface tension** and/or **surface energy**.
- The common **attraction forces** are dispersion forces, polar forces, induction forces etc.).
- The connection between **surface tension, γ,** and **surface energy, G^{S}**, and the precise meaning of both can be seen from thermodynamic considerations given above:

$$\gamma = G^{\mathrm{S}} + A\left(\frac{\partial G^{\mathrm{S}}}{\partial A}\right)_{\mathrm{TP}}$$

where: $G^{\mathrm{S}} = \gamma$, if G^{S} does not change as the area increases;
$G^{\mathrm{S}} \neq \gamma$, if G^{S} changes with the area.

Terminology

- **Note 1:** ***The concept of surface energy*** *is given either in terms of* ***Helmholtz function,*** *developed by some authors by supposing the* **surface *film to be stretched at constant temperature and volume****, or* ***Gibbs function*** *considering the* **constant temperature and pressure***.*

\- ***IUPAC recommends using one of the two terms for surface energy.***

- **Note 2:** ***The Gibbs function of surface energy , G*** ^{S}**, is independent of area and equals to surface tension***, if the local environment of the surface atoms remains the same when area is increased (as in a* **single component liquid***); in a* **solid** *or in a multi-component liquid the* **situation is different** *due to the* **plastic deformation of a solid surface***, or orientation of molecules and changes of interactions.*

- **Note 3:** ***The values for Gibbs function of surface energies and/or surface tension of solids (e.g. polymers)*** *in* ***practical*** *context are used as* ***inter-changeable terms.***

Surface phenomena, *cont.*

Practical usage of surface energy

- In many **practical** context, including adhesion, the values for **surface energies of solids (e.g. polymers)** cannot be measured with sufficient precision to make distinction between **‘surface energy’** and **‘surface tension’**.

- The **both terms** are used as **inter-changeable terms** with symbol commonly used for both, γ, with **equivalent units**: **Nm^{-1}** (Newton per metre) and/or **Jm^{-2}** or **mJm^{-2}** (Joul per square metre).

- **Solids** are usually classified as **‘high energy surfaces’** (e.g. metals and their oxides, ceramics of hundreds or thousands mJm^{-2}) and/or **‘low energy surfaces’** (e.g. organic surfaces, especially **polymers** with surface energy up to about 100 mJm^{-2}).

Surface phenomena, *cont.*

Interfacial tension (with only dispersion forces: $\gamma = \gamma^{\mathbf{d}}$)

- **Surface** cannot exist on its own – it is a **part of an interface between two phases** (A and B) (even if one phase is vacuum):

- **Interfacial tension (** γ_{AB} **)** between phases if surface tension of phases, γ_A and γ_B in equation is given as the geometric mean term:

$$\gamma_{AB} = \gamma_A + \gamma_B - 2\phi\left(\gamma_A\gamma_B\right)^{1/2}$$

where ϕ is a Good-Girifalco interaction parameter. If dispersion forces are dominant bonds in both phases A and B the molecules are similar in properties and ϕ will be close to unity.

Interfacial tension
(extension to polar components: $\gamma = \gamma^{\mathbf{d}} + \gamma^{\mathbf{p}}$)

- The **interfacial tension is further lowered** by the existence of other **(polar) forces that act at the interface**:

$$\gamma_{\mathrm{AB}} = \gamma_{\mathrm{A}} + \gamma_{\mathrm{B}} - 2\left(\gamma_{\mathrm{A}}^{\mathrm{d}}\gamma_{\mathrm{B}}^{\mathrm{d}}\right)^{1/2} - 2\left(\gamma_{\mathrm{A}}^{\mathrm{p}}\gamma_{\mathrm{B}}^{\mathrm{p}}\right)^{1/2}$$

Fowkes suggests that the principal non-dispersion interactions are not polar than acid-base (ab) interactions :

$$\gamma = \gamma^{\mathrm{d}} + \gamma^{\mathrm{ab}}$$

Lifshitz-van der Waals forces (LW) represent all the van der Waals interactions (in earlier terminology), that is a sum of dispersion and polar forces:

$$\gamma^{\mathrm{LW}} = \gamma^{\mathrm{d}} + \gamma^{\mathrm{p}}$$

Surface phenomena, *cont.*

Interfacial tension

(extension to acid base interaction: $\gamma = \gamma^{\mathbf{LW}} + \gamma^{\mathbf{ab}}$)

- **Acid-base approach** introduces the concept of a Lewis acid parameter of surface energy (γ^+), and Lewis base parameter of surface energy (γ^-).

\- **The interfacial tension** can be expressed:

$$\gamma_{AB} = \gamma_{\mathrm{A}} + \gamma_{\mathrm{B}} - 2\left(\gamma_{\mathrm{A}}^{\mathrm{LW}} \gamma_{\mathrm{B}}^{\mathrm{LW}}\right)^{1/2} - 2\left(\gamma_{\mathrm{A}}^{+} \gamma_{\mathrm{B}}^{-}\right)^{1/2} - 2\left(\gamma_{\mathrm{A}}^{-} \gamma_{\mathrm{B}}^{+}\right)^{1/2}$$

\- The acid base components of surface energy will be zero if the material is either mono-functional ($\gamma^+ = 0$ or $\gamma^- = 0$) or inert ($\gamma^+ = \gamma^- = 0$).

Surface phenomena, *cont.*

Interfacial tension, *cont.*

- **Interfacial tension (energy of an interface)** between phases A and B is related to the **surface energy of phases:**

\- **The interface** between phases **is stable** when:

$$\gamma_{\mathrm{AB}} \langle \gamma_{\mathrm{A}} + \gamma_{\mathrm{B}}$$

$$\gamma_{\mathrm{AB}} = \gamma_{\mathrm{A}} + \gamma_{\mathrm{B}} - \Delta$$

where Δ depends on the type of bonding across the interface (dispersion forces, dispersion and polar forces, LW and acid base forces etc.).

Surface energy, γ, and work of adhesion, W_a

- **Surface energy** (γ) and thus the **work of adhesion** (W_A) represent the **sum of components associated with the types of bonding** in accordance to the chemical nature of the material:

$$\gamma = \gamma^{d} + \gamma^{p} + \gamma^{h} + \gamma^{ab} + \ldots$$

$$W_A = W_A^{d} + W_A^{p} + W_A^{h} + W_A^{ab} + \ldots$$

where the superscripts refer respectively to dispersion force (d), polar force (p), hydrogen bonding (h), acid-base interactions (ab) etc.

Surface phenomena, *cont.*

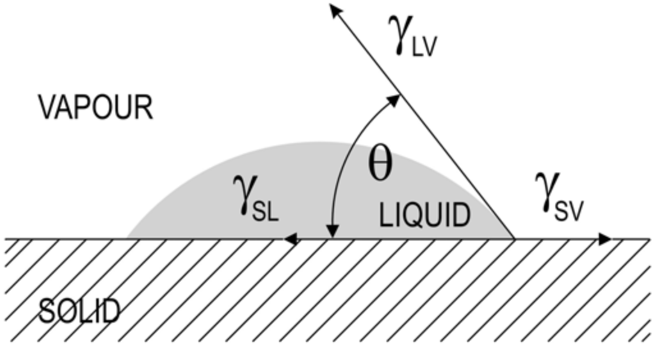
Wetting and spreading

- **Interfacial tension or a free interfacial energy** can be attributed to each interface between solid (S), liquid (L) and its vapour (V) i.e. interface **solid-liquid (γ_{SL}), solid-vapour (γ_{SV}) and liquid-vapour (γ_{LV})**.

  A force (per unit length) of triple line acts along each interface (using the mechanical tension definition).

- In order to assure **equilibrium**, a horizontal force balance must exist with a **defined contact angle (Θ)** measured between **solid-liquid interface** as is described by Young equation:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \Theta$$



Wetting, spreading and work of adhesion, *cont.*

- If the **Young equation** is used to **describe a system in equilibrium**:

$$\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}} = \gamma_{\mathrm{LV}} \cos\Theta$$

and combined with **Dupre's equation for work of adhesion:**

$$W_{\mathrm{A}} = \gamma_{\mathrm{SV}} + \gamma_{\mathrm{LV}} - \gamma_{\mathrm{SL}}$$

an alternative **Young-Dupre equation** that shows there is a **relationship between the size of contact angle and the forces of adhesion:**

$$W_{\mathrm{A}} = \gamma_{\mathrm{LV}}\left(1 + \cos\Theta\right)$$

Wetting, spreading and work of adhesion, *cont.*

- The term **'surface energy'** applies strictly for the **substance in contact with vacuum,** γ_S **,** in comparison to the surface in contact with vapour, γ_{SV} .
- **The reduction of surface energy of the solid** covered by a layer of vapour has been defined by an **equilibrium spreading pressure :**

$$\pi_S = \gamma_S - \gamma_{SV} = \mathrm{RT}\int_0^{p_o} \Gamma \mathrm{d}(\ln p) \qquad \pi_S = W_A^1 - W_A$$

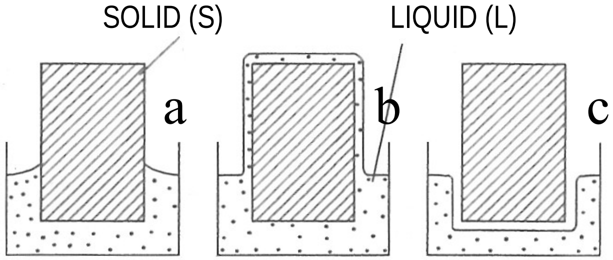
where p and p_0 are vapour pressure and equilibrium vapour pressure, R is the gas constant, T is the absolute temperature and Γ is the surface concentration of adsorbed vapour ($W_A{}^1$ is the work of adhesion in vacuum).

Notice: The **difference** due to the effect of **spreading pressure** on low energy polymer surfaces in practice is **usually neglected**.

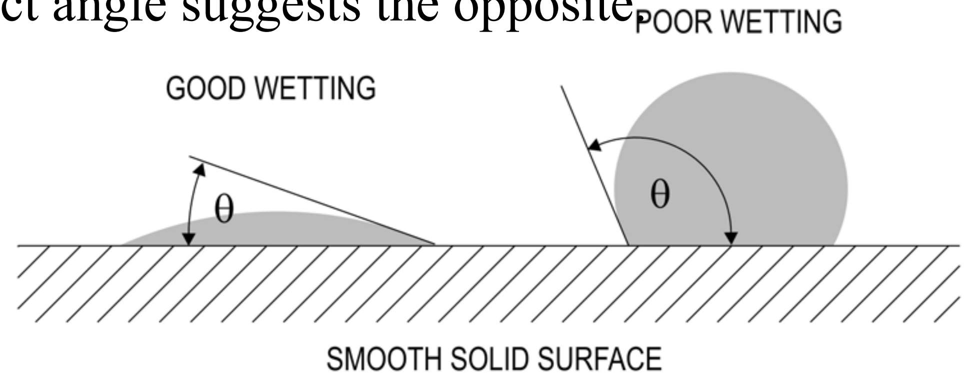
Surface phenomena, *cont.*

Wetting, spreading and dewetting

- **Description of wetting (a), spreading (b) and dewetting (c)** :



- A good experimental **example** of the **importance of surface chemistry** is the **contact angle** of water (or other liquids) **on a plastic surface**: the low contact angle indicates mutual attraction that lower the interfacial energy and the high contact angle suggests the opposite



Wetting, spreading and dewetting , *cont.*

- **The free energies of adhesion, wetting and spreading on the solid surfaces** are expressed in terms of the free energies, γ, of each interface between solid (S), liquid (L) and vapour (V):

- **Work of adhesion:**

$$W_{\mathrm{aSLV}} = \gamma_{\mathrm{SV}} + \gamma_{\mathrm{LV}} - \gamma_{\mathrm{SL}}$$

- **Wetting conditions:**

$$\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}} / \gamma_{\mathrm{LV}} \langle 1$$

(Affinity between S and L)

$$W_{\mathrm{eSVL}} = \gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}}$$

- **No wetting conditions:**

$$\gamma_{\mathrm{SV}} \leq \gamma_{\mathrm{SL}} - \gamma_{\mathrm{LV}}$$

(Lack of affinity between S and L)

$\theta = \pi$ $\quad \pi =$ disjoining pressure

- **Spreading conditions:**

$$\gamma_{\mathrm{SV}} \geq \gamma_{\mathrm{SL}} - \gamma_{\mathrm{LV}}$$

$$\theta = 0$$

$$W_{\mathrm{cSVL}} = \gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}} - \gamma_{\mathrm{LV}}$$

(positive S = spreading; negative S = no spreading; zero S = equilibrium)

Surface characteristics and contact angles

- **Wetting, spreading and adhesion phenomena** are often discuss in **correlation with contact angles of a liquids on a given surface:**

- Common **description of <u>surfaces</u>** as being ‘**rough**’ (porous, heterogeneous, contaminated with patches of material of differing surface energy, with adsorbed surface-active contaminants etc.) or **‘smooth’**.
- ‘**Clean**’ smooth **<u>plastic surfaces</u>** are **difficult to maintain** in industrial processes. Even a **low energy polymeric materials pick up contaminations** from the environment or the process used in their manufacture. If such a layer, even present only as a **monolayer** is **not removed**, it can act as a **‘weak boundary layer’** and seriously **disturb the adhesion** with other phase (adhesive, polymer, metal oxide etc.)
- **Hydrophobic polymers as low-energy solids** do not encourage spreading of liquid (thus they need some **surface pre-treatments**).

Surface phenomena, *cont.*

Surface inhomogeneity and contact angles

- The **principle of measuring both advancing and receding angles** and using their **arithmetic mean as the thermodynamic mean** is justified **only** when hysteresis is produced by a **regular array of inhomogeneities** such as with **certain types of roughness.**

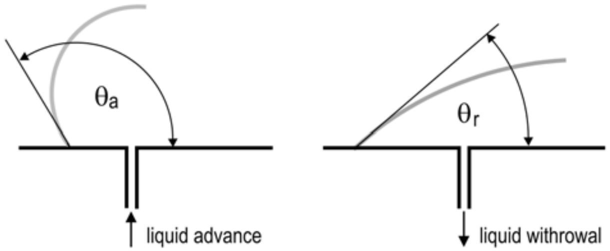
- The effect of **roughness of the solid surface** is to **increase the actual area of contact** between solid and liquid but also to **increase the un-wetted solid** per unit geometric area: when $\Theta < 90°$ the increased roughness **improve wetting** $\Theta \ll 90°$ **;** for $\Theta > 90°$ the increased roughness **lowered wetting**, $\Theta \gg 90°$.
- The **roughness factor**, ***r*** , proposed by Wenzel modifies Young's equation:

$$r\left(\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}}\right) = \gamma_{\mathrm{LV}} \cos\Theta$$

Surface phenomena, *cont.*

Surface inhomogeneity and contact angles, *cont.*

- All **practical surfaces** are **rough** on the molecular scale and of **fractal** nature.
- True **equilibrium contact angles are observed seldom** (even a ‘clean’ surface may be heterogeneous).
- Unseen surface **inhomogenity** very often occur at a microscopic level and cause **variations of contact angle** according whether the liquid is advancing (Θ_a), or receding (Θ_r). Contact angle hysteresis represent the difference between Θ_a and Θ_r ; $\Theta_{hyst} = \Theta_a - \Theta_r$



- It is an accepted practice, to relate **‘advanced’ contact angles to wettability** and **‘recessed’ contact angles to adhesion** properties of a three-phase system.

Surface characterization by contact angles

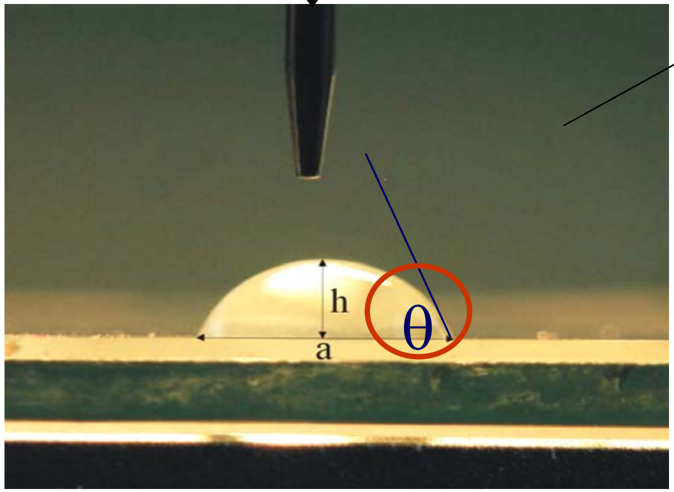
- **Surface tension of a liquid**, γ_{LV}, may be measured **directly** (Wilhelmy plate, capillary rice).
- **Surface tension of a solid** may be measured by **indirect methods** by **wetting of the solid surface** by reference **liquids** and **measuring the equilibrium contact angle** of a liquid drop on the given surface:

Test liquids of known

$$\gamma_{\mathrm{L}} = \gamma_{\mathrm{L}}^{\mathrm{d}} + \gamma_{\mathrm{L}}^{\mathrm{p}}$$

(water, formamide, diodomethane...)

↓



$$\theta \rightarrow \cos\theta$$

↓

Models for γ_{SL}

(geometric and/or harmonic mean)

↓

Combination with Young's eq.

↓

Determination of $\gamma_{\mathrm{SV}}^{\mathrm{d}}, \gamma_{\mathrm{SV}}^{\mathrm{p}} (\gamma_{\mathrm{SV}} = \gamma_{\mathrm{SV}}^{\mathrm{d}} + \gamma_{\mathrm{SV}}^{\mathrm{p}})$

Surface phenomena, *cont.*

Surface characterization by contact angles, *cont.*

- **Owens-Wendt model** : interfacial surface energy, γ_{SL}, represents the **geometric mean** of **surface energy of solids** (e.g. **polymers**), γ_{SV} , and various test liquids of known $\gamma_{\mathrm{LV}}^{\mathrm{d}}$ and $\gamma_{\mathrm{LV}}^{\mathrm{p}}$ in contact:

$$\gamma_{\mathrm{SL}} = \gamma_{\mathrm{SV}} + \gamma_{\mathrm{LV}} - 2\left(\gamma_{\mathrm{SV}}^{\mathrm{d}}\gamma_{\mathrm{LV}}^{\mathrm{d}}\right) - 2\left(\gamma_{\mathrm{SV}}^{\mathrm{p}}\gamma_{\mathrm{LV}}^{\mathrm{p}}\right)^{1/2}$$

$$\gamma_{\mathrm{LV}}\left(1+\cos\Theta\right) = 2\left(\gamma_{\mathrm{SV}}^{\mathrm{d}}\gamma_{\mathrm{LV}}^{\mathrm{d}}\right) + 2\left(\gamma_{\mathrm{SV}}^{\mathrm{p}}\gamma_{\mathrm{LV}}^{\mathrm{p}}\right)^{1/2}$$

- **Wu model**: interfacial surface energy, γ_{SL}, represents the **harmonic mean** of surface energy of phases γ_{SV} and γ_{LV} in contact;

$$\gamma_{\mathrm{SL}} = \gamma_{\mathrm{SV}} + \gamma_{\mathrm{LV}} - \frac{4\gamma_{\mathrm{SV}}^{\mathrm{d}}\gamma_{\mathrm{LV}}^{\mathrm{d}}}{\gamma_{\mathrm{SV}}^{\mathrm{d}} + \gamma_{\mathrm{LV}}^{\mathrm{d}}} - \frac{4\gamma_{\mathrm{SV}}^{\mathrm{p}}\gamma_{\mathrm{LV}}^{\mathrm{p}}}{\gamma_{\mathrm{SV}}^{\mathrm{p}} + \gamma_{\mathrm{LV}}^{\mathrm{p}}}$$

$$\gamma_{\mathrm{LV}}\left(1+\cos\Theta\right) = \frac{4\gamma_{\mathrm{SV}}^{\mathrm{d}}\gamma_{\mathrm{LV}}^{\mathrm{d}}}{\gamma_{\mathrm{SV}}^{\mathrm{d}} + \gamma_{\mathrm{LV}}^{\mathrm{d}}} + \frac{4\gamma_{\mathrm{SV}}^{\mathrm{p}}\gamma_{\mathrm{LV}}^{\mathrm{p}}}{\gamma_{\mathrm{SV}}^{\mathrm{p}} + \gamma_{\mathrm{LV}}^{\mathrm{p}}}$$

Surface characterization by contact angles, *cont.*

- For the case of **solid polymers** a certain simplification can be made: the **critical surface tension** can be determined by measuring the contact angles (Θ) of the series of liquids of decreasing surface tension (γ_{LV}) and plotting a graph of cosΘ vs. γ_{L} and extrapolation to cos$\Theta = 1$.
- **Critical surface tension of the solid,** γ_{C} **,** corresponds to the value of surface tension of a liquid that will spread spontaneously (cos$\Theta = 1$), assuming negligible spreading pressure ($\pi_{\mathrm{S}} = \gamma_{\mathrm{S}} - \gamma_{\mathrm{SV}} = 0$).
- From Young's equation:

$$\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}} = \gamma_{\mathrm{LS}} = \gamma_{\mathrm{C}} \qquad \gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}} = \gamma_{\mathrm{C}}$$

where γ_{SL} between a polymer and an organic liquid is generally low:

$$\gamma_{\mathrm{C}} \cong \gamma_{\mathrm{SV}} \cong \gamma_{\mathrm{S}}$$

Summary

- **Surface energy of polymers** (commonly low), γ_{SV}, is both **temperature and composition dependent and needs surface pre-treatments:**
  γ_{SV} **decreases with temperature** (measurements of γ_{SV} at constant temperature);
  γ_{SV} **changes with composition** of mixture at the surface and may alter wetting coefficient, ***S***, for a given solid – liquid system i.e. **favour wetting** by selected composition or **disfavour wetting** by different surface contaminations.
- **Wetting thermodynamics** assure the **intimate molecular contact** possible only with 'clean' surfaces.
- **Wetting kinetics** depend on (low) **viscosity** of liquid (e.g. adhesive) and on **topography** (surface texture) of surface (e.g. substrate).
- **Interfacial adhesion is simply wetting and setting by interfacial bonds!**

Adhesion phenomena

Adhesion – phylosophy

- Adhesion – from ‘*adhaerere’* (‘ to stick to’)
- *Phylosophy* (theory) of adhesion by Plato (cit. from K.L. Mittal):

IT IS NOT POSSIBLE FOR ***TWO THINGS TO BE FAIRLY UNITED***
WITHOUT A THIRD,
FOR ***THEY NEED A BOND BETWEEN THEM*** *WHICH*
SHALL JOIN THEM BOTH,
THAT AS THE FIRST IS TO THE MIDDLE,
SO IS THE MIDDLE TO THE LAST
THAN SINCE ***THE MIDDLE BECOMES THE FIRST AND THE LAST,***
AND THE LAST AND THE FIRST BOTH BECOME MIDDLE,
OF NECESSITY ALL WILL COME TO BE THE SAME,
AND BEING THE SAME WITH ONE ANOTHER,
ALL WILL BE A UNITY.

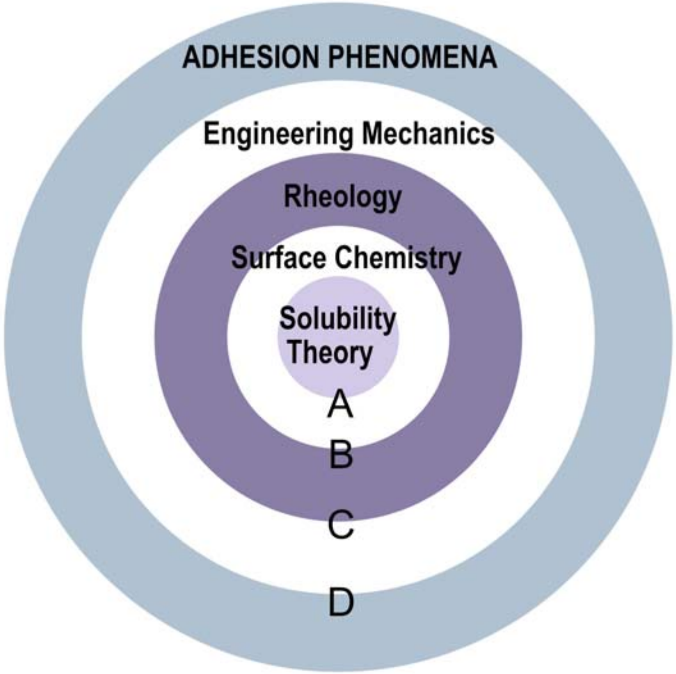
Adhesion – definition and theories

- **Adhesion considerations** are essentially concerned on **joining together** two dissimilar (or similar) materials:

- **ASTM D 907 definition of 'adhesion'** as a state in which two surfaces are held together by interfacial forces, which may consist of valence forces or interlocking forces or both.
- The **particular adhesion** (e.g. bonding porous substrates, smooth surfaces, electrically charged surfaces, inert polymer surface etc.) **for building the various theoretical models** (**theories of adhesion**)
- **Study of adhesion** is concerned on the process or material **variables that effect the interface** in order to **optimise the variables and interface** region between the two phases (and the opposite- adhesion might be the unwelcome event – e.g. at injection moulding that needs release agent etc).

Adhesion science

- **Science of adhesion** involve other more traditional disciplines represented by Kaeble's hierarchy of the scientific disciplines that contribute to the **rationalisation of adhesion phenomena**:



where A= theory of solubility, B= theory of interfaces; C= theory of fracture; D= mechanics model of phenomena

Adhesion science, *cont.*

- **Adhesion science** represent simply the **interactions** that must be considered, if we are to **understand** completely the **response** of the system in which **adhesion plays an important role**:

- At the **molecular level** one must appreciate the way in which **organic molecules** may **interact with substrate** (inorganic and/or organic one);
- **Inorganic phase** - less mobile phase i.e. metal substrate (adherent) covered with oxide layer, or carbon, or glass fibres, or inorganic fillers etc.
- **Organic phase –** more mobile phase i.e. adhesive, or organic coating, or polymer matrix in filled composites, blends etc. (e.g. epoxy resins might be used as adhesive, coating and/or polymer matrix in composite.

Adhesion science, *cont.*

- One should be able to **identify analytically** those **molecular species** which may have a beneficial or deteriorative effect on adhesion.

- **Design of bonded joint** or **coated adherent** etc.

- In order to **rationalise the adhesion phenomena** the all aspects of **surface and interface science**, **polymer physics, chemistry an rheology** and **fracture mechanics** have to be considered.

Adhesion phenomena, *cont.*

Adhesion – fundamental and practical

- **Conclusions on the satisfactory level of adhesion depend on:**
- **Intimate contact** at a molecular level;
- **Successful pre-treatment** of the substrate to remove contaminations and/or to enhance binding by incorporation the chemical species;
- **Mechanisms of adhesion** that will be dominant;
- **Parameters** that will **effect adhesion** (both chemical and mechanical);
- **Testing of bonding** (mechanical perturbation, environment effect, adhesive strength degradation with time in aggressive environment);
- **Kinetics of failure** (defining the locus of failure at an atomic or molecular level);
- **Surface sensitive analysis methods** to define the surface layers important for good or lack of adhesion.

Adhesion – fundamental and practical, *cont.*

ADHESION AS AN ‘UMBRELLA’ FOR SURFACE PHENOMENA

Wetting and spreading,

Interfacial energy , Work of adhesion,

Failure mechanisms

Interactions between fillers, fibres etc. with matrix

Surface pre-treatments and surface characterisations

ADHESION AS A BASE FOR

Adhesive joints

Adhesive materials: adhesives, coatings, sealants, dyes

Filled polymer composites and blends

Nanomaterials

Adhesion phenomena, *cont.*

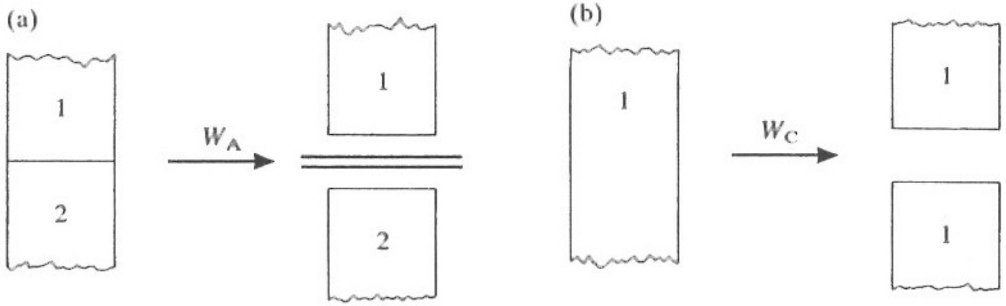
Adhesion – fundamental and practical, *cont.*

- **Fundamental adhesion** refers to the **forces between atoms at the interface**:

- **Theories of adhesion** applied to the particular interface;
- Expressed in **terms of forces** (Nm^{-1}) or **in terms of energies** (mJm^{-1});
- Calculated from **a theoretical model**;
- **Thermodynamic work of adhesion** as a **'fundamental'** measure of adhesion is defined as a free energy change required to separate different phases 1 and 2 and/or the same phases i.e. **work of cohesion:**

$$W_A = \gamma_1 + \gamma_2 - \gamma_{12}$$

$$W_C = 2\gamma_1$$



Adhesion phenomena, *cont.*

Adhesion – fundamental and practical, *cont.*

- **Fundamental adhesion** refers to the **forces between atoms at the interface**:
- **Coefficient of spreading for phase 1 and 2 in contact at interface :**

$$S=\gamma_1+\gamma_2-\gamma_{12} \quad (\Theta=0) \qquad\qquad S=W_\mathrm{A}-W_\mathrm{C}$$

- The use of expressions above requires connections with **Young's equation**.
- The **higher value of a spreading coefficient** between particular phases 1(substrate) and 2(adhesive), the **greater is the thermodynamic work of adhesion,** W_A compared to the cohesive energy of adhesive, W_C i.e. **high value of *S*** will favour **cohesive failure** within adhesive and **more reliable adhesive bond.**

Adhesion – fundamental and practical, *cont.*

- **Practical adhesion** refers to the results of the various **tests of adhesion** of **adhesive joint or coating or composites** such are **shear, peel, tensile strength** obtained from the related tests:

- **Numerical results** from the particular test depend on the **operational variables** (dimensions of the test piece, rate of loading etc.);
- **Adhesion** reflects not only **fundamental adhesion at the interface** but also the **mechanical response** of the **adhesive, substrate and interfacial region.**

- **Practical adhesion = *f* (Fundamental adhesion, other factors)**

Adhesion phenomena, *cont.*

Adhesion – fundamental and practical, *cont.*

- **Mode of failure** in a practical test of adhesion may be **adhesive, cohesive or mixed:**

\- All **practical tests** give a number that **reflects indirectly the interfacial forces and fundamental adhesion.**

\- **Peel energy, *P*** (measured in 90° peel test) could be expressed:

$$P = F / b = W_{\mathrm{A}} \left[\mathrm{or}\ W_{\mathrm{C}}\right] + \psi_{\mathrm{plast}} + \psi_{\mathrm{v/e}} + \psi_{\mathrm{bend}} + \ldots$$

where F is measured peel load of a peeled strip of width b;

P is a measure of work of adhesion (W_A) or work of cohesion (W_C), rheology in terms of energy dissipated in plastic deformation (ψ_{plas}), in viscoelastic loss ($\psi_{\mathrm{v/e}}$), in bending (ψ_{bend}) etc.

Adhesion – fundamental and practical, *cont.*

- **Tensile tests and shear tests** measure a critical stress rather than energy of fracture:

- Griffith-Irwing theory of fracture adopted by Good:

$$\sigma_{\mathrm{f}} = k\left(EG/l\right)^{1/2}$$

where σ_{f} is a fracture stress of material of modulus E, k is a constant, l is the length of the critical crack and G is the work of fracture per unit area:

$$G = W_{\mathrm{A}}\left[\mathrm{or}\ W_{\mathrm{C}}\right] + \psi$$

- Depending on the locus of failure, either work of adhesion, W_{A}, or the work of cohesion, W_{C}, or both is responsible for a failure, ψ represents all the other energy dissipation terms.

Adhesion phenomena, *cont.*

Adhesion – fundamental and practical, *cont.*

- **Failure at the stress** σ_f will occur where the term (EG / l) has the minimal value, i.e. at the interface (**interfacial**) or within the bulk (**cohesive**) or close to the interface (**combined**).

- **Viscoelasticity of polymer materials** is important in considerations the kinetic effects i.e. effects of **test rate on adhesion, effect of substrate, creep failure and environmental failure.**

- **Failure in composites, or de-bonding the adhesive joint** will be always at the **weakest point – at the interface and/or in the bulk** giving us the indirectly the **information's about the strength of interactions at the interface.**

Adhesion phenomena, *cont.*

Adhesion theories

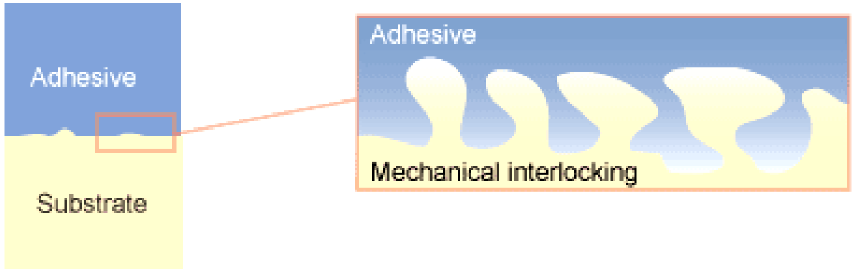
- **The first requirement for a <u>successful bond between two phases</u>** is to establish **contact at a molecular or atomic level** (e.g. substrate and an over-layer such as metal and adhesive or organic coating; vacuum deposited metal on polymeric substrate, or polymer on polymer etc.).
- **Potential level of adhesion** depend on the **possible interactions** that may occur i.e. on the **potential mechanisms of adhesion**.
- **Very wide range of substrates and the mobile phases of various adhesive materials** are in use and there is **no unique mechanisms of adhesion** applicable to all adhesion cases.
- **Particular case of adhesive bonding** needs to be studied and explained.

Adhesion phenomena, *cont.*

Mechanical theory

- **Mechanical theory** is the oldest one but supported with many practical evidence, i.e. adhesive strength, bond durability and related parameters is proportional to the surface roughness. Theory **involve interlocking** of the solidified adhesive with the **roughness and irregularities** of the surface

  (e.g. valid on a **macro scale for fibrous materials** such are paper, leather, wood etc.)



- Increased roughness provides more surface area over which bonds can form but **mechanical adhesion** is very rare the only mechanism involved.

***Important for the increased adhesive strength*: increased roughness, porosity, size compatibility.**

Mechanical theory, *cont.*

- **The mechanical concept** may be considered on **two different scale**:

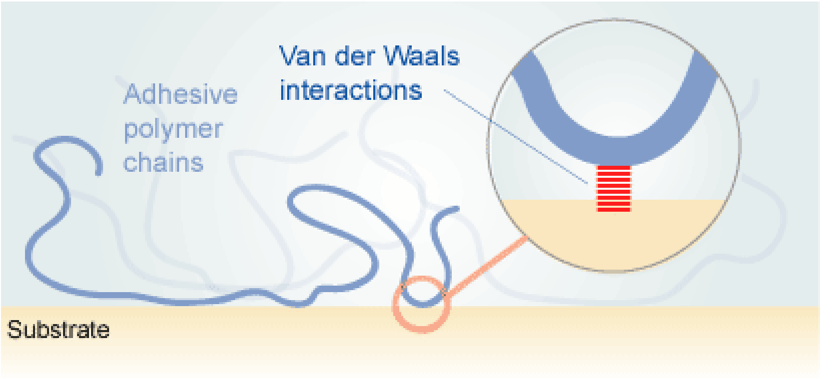
- **Interlocking on a macro scale**: e.g. **plastics** (ABS, HIPS) previously etched with chromic acid that removes elastomer from the surface layer and leave a porous structure, **coated with thin layer of metal** (Cu) deposited by chemical reduction; **two mechanisms are involved** i.e. chemical bonding between metal and plastic and mechanical interlocking between the metal and the porous plastic surface.

- **Interlocking on a micro scale**: e.g. **penetration of polymer** into micro-pores of **porous layer of aluminium oxide** obtained by aluminium anodizing in an acidic electrolyte that allow the **mechanical interlocking**.

Adhesion phenomena, *cont.*

Adsorption theory

- **Adsorption theory** is the most relevant for adhesion between **inorganic and organic systems** – intimate contact **at the interface** is necessary to provide adhesion through the **intermolecular forces** that exist between atoms, molecules and ions of the two phases depending on the bonds energy (kJ/mol): ionic (600-1100), covalent (60-700), metallic (110-350), Bronstead acid-base (up to 1000), hydrogen (up to 40), van der Waals (4-20) etc.



- The bond types may be classified into **primary bonds (**ionic, covalent, metallic) and **secondary bonds** (van de Waals etc.) on the basis of the magnitude of bond energy.

Adhesion phenomena, *cont.*

Adsorption theory, *cont.*

- **For the quantitative assessment of interfacial bonds** it is necessary to be able to estimate the interfacial free energy, γ_{ab} , between an inorganic (a) and organic component (b) in contact at the interface in order to calculate the **work of adhesion, W_{A}:**

$$W_{\mathrm{A}} = \gamma_{\mathrm{a}} + \gamma_{\mathrm{b}} - \gamma_{\mathrm{ab}}$$

\- The attractive constants (A) between like (aa) and unlike (ab) molecules:

$$A_{\mathrm{ab}} / (A_{\mathrm{aa}} A_{\mathrm{bb}})^{1/2} = 1$$

\- The relationship was set equal to ϕ rather than unity with maximum, $\phi = 1$:

$$\gamma_{\mathrm{ab}} = \gamma_{\mathrm{a}} + \gamma_{\mathrm{b}} - 2\phi(\gamma_{\mathrm{a}}\gamma_{\mathrm{b}})^{1/2} \qquad W_{\mathrm{A}} = 2(\gamma_{\mathrm{a}}^{\mathrm{d}}\gamma_{\mathrm{b}}^{\mathrm{d}})^{1/2} + 2(\gamma_{\mathrm{a}}^{\mathrm{p}}\gamma_{\mathrm{b}}^{\mathrm{p}})^{1/2}$$

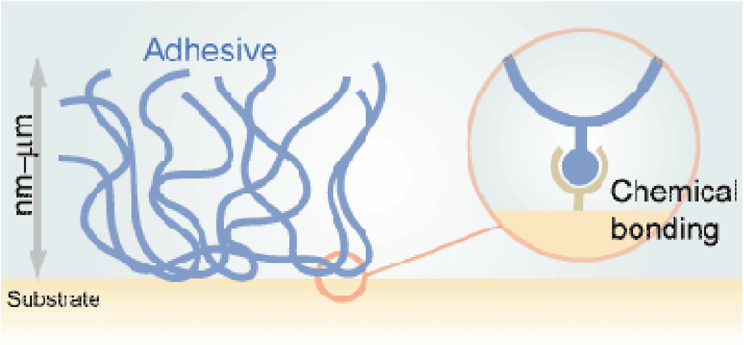
\- ***Important for the increased adhesive strength*:**

spontaneous wetting ($\gamma_{\mathrm{b}} \langle \gamma_{\mathrm{a}}$) max. surface contact, min. stress concentrations, use of 'primers'.

Adhesion phenomena, *cont.*

Chemical theory

- **Chemical theory** involves **primary chemical bonds** (covalent or some ionic character) that provide a separate contribution to the adhesive bond (in addition to dispersion forces).



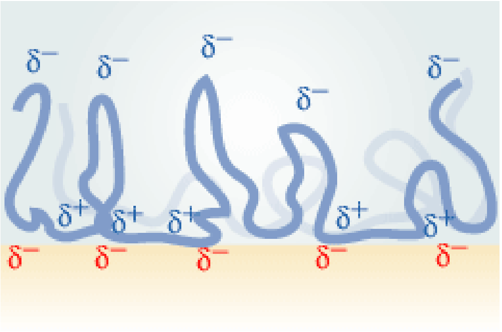
- **Sophisticated surface analytical techniques**, available within the past two decades, is necessary for the recognition of the **chemical bonds at the surface** by identifying the fragments of bonding compounds within the fractured surfaces of the broken bonds.

Important for the increased adhesive strength: crosslinking by using a second component (hardener).

Adhesion phenomena, *cont.*

Electrostatic theory

- **Electrostatic theory** is based on the existence of an **electrical double layer at the interface** (e.g. between metal and polymer). Sufficiently close contact between two material with different band structures allows some electron transfer treating the interfacial region of a joint as a parallel plate capacitor.

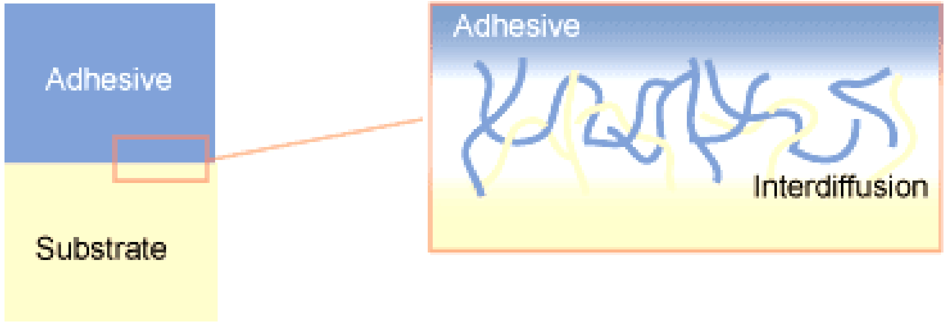


\- Electrostatic forces across the double layer could contribute to the total adhesive bond strength.

Adhesion phenomena, *cont.*

Diffusion theory

- **Diffusion theory** explains **inter-diffusion of the two interacting material** bringing adhesion between them.
- For the specific case of **two similar polymers in contact** below their glass transition there may be an interaction via **diffusion of polymer chain ends or segments** across the interface.



- **Inter-diffusion** of the two polymers requires a degree of **chain mobility** and **mutual solubility** with both phases in **amorphous state** (e.g. auto-adhesion or solvent welding of amorphous polymers).

Other theories

- **Weak boundary layer theory (WBL)** explains the premature adhesive failure due to the existence of WBL's at the surface (e.g. grease, contaminants, segregations of specific components at the interface, incorrect pre-treatment procedure, environmental exposure, included air due to the incorrect wetting etc).

- **Pressure sensitive adhesion of tapes** depend on the continuing presence of a layer of a very viscous liquid between the tape and the surface.
- This viscous liquid (adhesive) is spread in a very thin layer.
- A considerable force is needed to remove the tape from the surface so long as the adhesive remains a viscous liquid.

Adhesion phenomena, *cont.*

Other theories, *cont.*

- **The most acceptable theory of adhesion**

$$\phi = \alpha\phi_{\mathrm{M}} + \beta\phi_{\mathrm{A}} + \gamma\phi_{\mathrm{C}} + \delta\phi_{\mathrm{E}} + \varepsilon\phi_{\mathrm{WBL}} + \eta\phi_{\mathrm{D}} + \theta\phi_{\mathrm{AB}} + \rho\phi_{\mathrm{R}} + \ldots \mathrm{w}\phi_{\mathrm{X}}$$

$$(\alpha^2 + \beta^2 + \gamma^2 + \delta^2 + \varepsilon^2 + \eta^2 + \theta^2 + \rho^2 + \ldots \mathrm{w}^2)^{1/2} = 1$$

where: M= mechanical theory, A= adsorption theory, C= chemical theory, E= electrostatic theory, WBL= weak boundary layer theory, D= diffusion theory, AB= acid-base theory, R= rheological theory, X = theory that will be developed…

Comparison of adhesion theories

Analysis

Theory:	**For:**	**Against:**
Mechanical	Porous, rough surface –needs etching (paper, textile, wood)	Flat nonporous surface (glass, metal, ceramics)
Adsorption	Intimate contact, wetting - needs molecular bonds (metal, ceramics)	Surfaces with inclusions such as air, contamination
Diffusion	Thermoplastics needs compatibility, kinetic mobility, above Tg	Cross-linked materials, bound polymer-metal, polymer-glass
Electrostatic	Glass-PVC	Incompatible material etc.

Adhesion theories in practice

- **Some practical examples (several adhesion mechanisms involved):**
- **Aluminium sheets bonded with an epoxy structural adhesive:**

  Al surface prepared by chemical etching – oxide layer with micro-pores increased roughness and chemical activity; epoxy adhesive in liquid state penetrate into the Al pores -**diffusion**, develop forces across the interface-**adsorption by London forces and –develop some primary chemical bonding.**

- **Wallpaper stuck to a plaster surface with water-based cellulose adhesive:** Adhesive penetrate into both surfaces – **diffusion,** water evaporate, solidifying adhesive and the texture – **interlocking,** some chemical bonds developed with the paper and the plaster **– chemical bonding.**

Polymer-polymer adhesion

Examples

- **Polymer-polymer interfaces and adhesion between them** plays a critical role in **determining the properties at polymer processing.**

- **Examples:**

- **Injection moulding** in polymer processing (plastic parts in automotive applications);

- **Extrusion** create **many interfaces** in the form of internal weld-lines where the fluid fronts coalescence and weld (for plastic pipe);

- **Compression moulding** and **sintering** requires **coalescence** of pellets or powder when their surfaces contact in the mould;

Polymer-polymer adhesion, *cont.*

Examples, *cont.*

- **Construction of composites** with thermoplastic matrices requires the fibre-filled laminated to weld by an **inter-diffusion process at the interface** (aircraft bodies);

- **Tack** between uncured rubber sheets by **welding** (auto tyre manufacture);

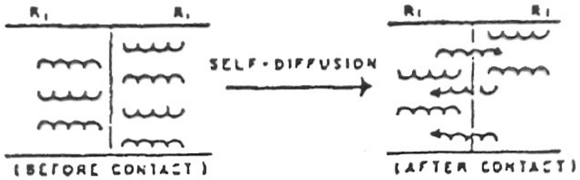
- **Drying** of latex paints and coatings include a very **large number of interfaces per unit volume** (latex particles of ca 1000 A **inter-diffuse** together to form a continuous film).

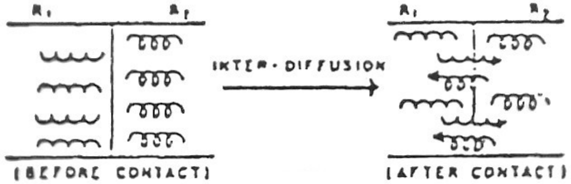
Polymer-polymer adhesion, *cont.*

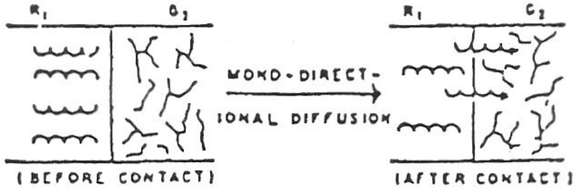
Examples, *cont.*

- **The <u>strength of polymer-polymer interface</u> i.e. the adhesion between two polymers** depends on the structure that develops during its formation.

\- **Example**: **Two amorphous polymers** that are brought into a **good contact above their glass transition. Compatibility** between polymers at an interface, underlined by **diffusion theory of adhesion,** depends on the ability of polymer chains at the interface to mix by **inter-diffusion**.





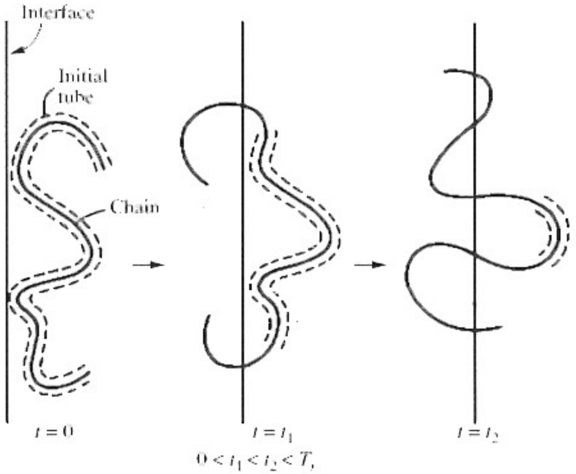


Polymer-polymer adhesion, *cont.*

Examples, *cont.*

- **Example**: **Polystyrene** welded to itself (**self-diffusion**) at 118 °C ;

  The **chain conformations at the interface** tend to relax towards those in the bulk because of Brownian motion: (1) short range Fickian diffusion of individual chain segments; (2) Rouse relaxation between chain entanglements; (3) Rouse relaxation of the whole chain; (4) Reptation diffusion; (5) Fickian long-range diffusion.



Polymer-polymer adhesion, *cont.*

Compatibility

- **Compatibility is a measure of two substances** (i.e. **polymers) to mix**.
- **Conditions of compatibility:** Gibbs free energy of mixing, ΔG_m , is negative.

$$\Delta G_\mathrm{m} = \Delta H_\mathrm{m} - T\Delta S_\mathrm{m}$$

where ΔH_m is enthalpy of mixing and ΔS_m entropy of mixing and T is absolute temperature.

Mixing always increases disorder and thus ΔS_m **is high and positive** that **lower ΔG_m** to the **negative term** and therefore **favours mixing.**

However, **ΔH_m term**, where polymers are involved in mixing is **commonly positive** that is **not favourable situation for mixing** where ΔH_m should be large and negative.

- The above approach is not practical for predict mixing or not (there is not collections of data).

Polymer-polymer adhesion, *cont.*

Compatibility, *cont.*

- **<u>Practical approaches to predict mixing of polymers</u>:**
- **To compare the chemical structures** i.e. 'like generally dissolves like'
- **To use solubility parameter, δ_S,** where ΔH_v is the molar heat of vaporisation and V is the molar volume:

$$\delta_S = \{[\Delta H_V - RT/V]\}^{1/2}$$

with the **enthalpy expression H_m:**

$$\Delta H_m = V\phi_1\phi_2(a_1^{1/2}/b_1 - a_2^{1/2}/b_2)^2$$

where ϕ 's are volume fractions, a and b are constants from van der Waals equation. **The closer the values of δ_S for two substances, the more likely they are to be compatible**.

Polymer-polymer adhesion, *cont.*

Compatibility, *cont.*

- **Polymer-polymer interface:**

- **Structure and strength of the interface** formed when two polymers are brought into good contact:

- **Weak interface –** if interpenetration is limited: chain pull-out and possible chain fracture may occur;
- **Strong interface –** if more extensive interpenetrations happened: extensive energy dissipation may occur with cohesive failure;
- **The strength of interface (A/B)** between **incompatible polymers A and B** can be **considerably increased** by using **compatibilizer**:

  (e.g. A-B block-copolymer with A block tending to diffuse into A and B block into B).

Polymer-polymer adhesion, *cont.*

Compatibility, *cont.*

- **The importance of compatibility in the context of adhesion:**
- **Examples:**

\- **Solvent-based adhesives** with selection of **'compatible' solvents**;

\- **Adhesive joint** will be **stable** in the presence of **'incompatible' liquid**;

\- **'Compatible' additives** in **adhesive compositions** will **improve the adhesive function** (plasticizers, antioxidants)

Notice*: *There might be a problem of migrating additives into the adhesive-substrate interface and forming a weak boundary layer (WBL).

Polymer-polymer adhesion, *cont.*

Compatibility, *cont.*

- **Compatibility between polymers at interface:**

- Depending on the **ability of polymer chains at an interface to mix by inter-diffusion** (underlined by **diffusion theory of adhesion** relevant in the **small number of cases** relating to auto-adhesion above Tg, or solvent welding, of both amorphous polymers);
- With **identical polymers at the each side of interface** there will be **complete mixing at thermodynamic equilibrium**;
- **Polymers** that are **chemically very similar** often **do not mix** because the entropy of mixing is usually negative (ΔS_m), but **enthalpies of polymer mixing** (ΔH_m) **are often small and positive** resulting in positive Gibbs free energy (ΔG_m).

Notice: thermodynamic incompatibility of polymers is a fundamental problem in making polymer blends.

Polymer surface modification

Surface pre-treatments of polymers (plastics)

- **Many industrial and consumer systems required a good adhesion to plastic surfaces** but the **inherent low energy of plastics** would make the process difficult without some form of **pre-treatment**.
- **Polymer surface pre-treatment** (e.g. prior to adhesive bonding, painting, printing, metallization etc.) in order to:
- **Remove the surface contamination** (surfactant, plasticizer, etc.)**;**
- **Enhance the surface energy of plastics** (initial non-polar hydrophobic surface)**;**
- **Lower the contact angle, improve wetting, increase work of adhesion;**
- **Surface activation** (introduction of functional groups, improve adhesion).

- **'Clean' smooth plastic surfaces** are difficult to maintain in **industrial processes and in environment – contaminants create the weak boundary layers (WBL) that should be removed from the surface.**

Surface pre-treatments of polymers (plastics), *cont.*

- **General aspects of pre-treatment to improve adhesion to low energy surfaces of plastics:**

- **Solvent pre-treatments** (e.g. with solvent ethyl acetate to remove the plasticizer from the surface of poly (vinyl chloride):
- Removal of **weak boundary layer/contaminants**;
- Increased **surface roughness/bond area**;
- **Plasticisation of surface** to aid the diffusion process.
- **Mechanical pre-treatments** (e.g. with abrasive pads to improve adhesion of thermo-reactive polymers):
- Removal of **weak boundary layer/contaminants**;
- Increased **surface roughness/bond area**;
- Increased possibility of **mechanical keying.**

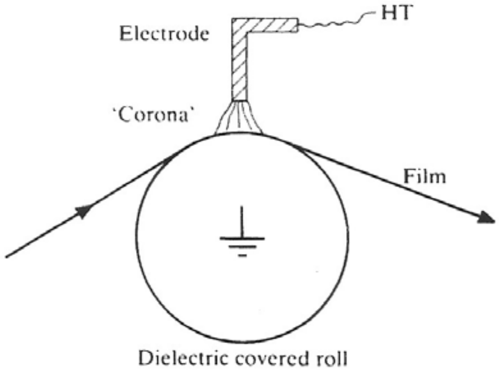
Polymer surface modification, *cont.*

Surface pre-treatments of polymers (plastics), *cont.*

- **Oxidative pre-treatments** (e.g. with chromic acid, ‘flame’, ‘corona discharge’ to improve bonding of low-density polyethylene):
- Removal of **contaminants and additives**;
- Change in **topography e.g. surface roughness (+ or -).**
- Alter **surface chemistry** (**introduction of functional groups**) to affect wetting and adhesion by **modifying the forces of attraction between plastic surface and other component.**
- **Surface ‘etching’ with ‘chromic’ acid:**
- There are **differences** between the material removed (etch rate), the depth and the extent of oxidation of **various polyolefins following chemical oxidation.**

Surface pre-treatments of polymers (plastics), *cont.*

- **'Corona' discharge treatment (CDT)** as the most widely used technique in industry, is suitable for continuous treatment of **plastic film** (LDPE, PET etc.) at **atmospheric pressure** where film passed between an earthed/insulated roller and an array of high voltage electrodes - at voltage peaks there is the electrical break up of **air molecules** which **ionize.**

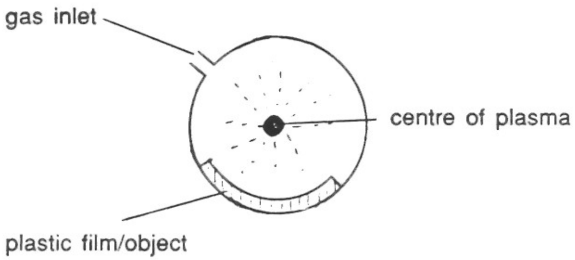


- The **mechanisms of surface modification**: change from C-C and C-H into C-N and C-O species (e.g. surface energy of PE increased from 31 to 50 mJm^{-2}).

Polymer surface modification, *cont.*

Surface pre-treatments of polymers (plastics), *cont.*

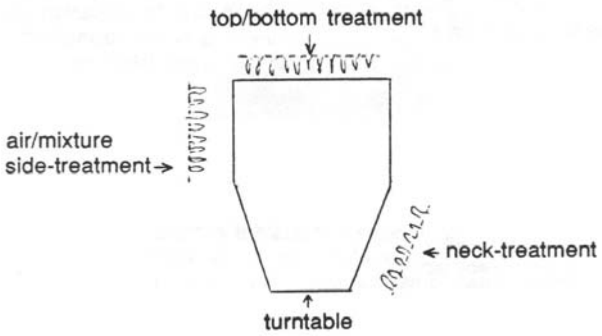
- **Plasma treatment –** much research with a wide variety of polymers have been made. Power is applied to a gas or a monomer (air, oxygen, nitrogen, argon etc.) in a **low vacuum chamber** and a **plasma formed consisting of ions, electrons, atoms and free radicals** does produce a more uniform **surface oxidation of plastics** compared to CDT .



- Various **mechanisms of surface modification:** ablation of small molecules, cross-linking or introduction of carbonyl and amine groups, possible grafting to the polymer surface with monomers.

Surface pre-treatments of polymers (plastics), *cont.*

- **Flame treatment** is preferable for treating ticker plastic objects (e.g. PE bottles prior to printing/labelling) as a surface oxidation method which relies on temperature (the gas-burners with 10% oxygen excess to that for complete combustion as hydrocarbon gas mixture).



- The exact **mechanisms of flame-treatment** is not known: mixture of processes- thermal oxidation as a chain-reaction free radical attack, surface oxidation and incorporating of oxygen and nitrogen groups.

Methods for polymer surface modification

- **Examples:**

- **Polyolefins (e.g. low-density polyethylene),** useful as **packing material** change (functionalize) the surface in order to **improve adhesion of printing** ink by **flame treatment, CDT, chromic acid treatment, plasma treatment**;
- **Polypropilene** is pre-treated by **flame treatment** in order to change surface structure and **improve the paint adhesion** especially under aggressive service conditions;
- **Polyurethane and poly (vinyl chloride)** are treated by **surface bombarding with carbon dioxide particles**;

Methods for polymer surface modification, *cont.*

- **Examples:**

- **Pre-treatment of composite** by the tear (peel) method where a **fabric incorporated in the composite near the surface is pulled away** just prior to bonding;
- **Fluorocarbon polymers** pre-treated with **powerful reducing agent** generated at the anode and cathode respectively of an electrochemical cell, that **significantly increase failure loads in adhesion tests**;
- **Polymerized coatings of organic polymers** deposited **by plasma polymerization** onto any substrate **with very much improved adhesion**: technique used to deposit polymeric coatings without damage to the polymeric substrate; polymers deposited from a plasma differ from those synthesized by conventional techniques – they are highly crosslinked with lack structural regularities with many different functional groups.

Polymer surface identification

Methods for polymer surface identification

- **Various methods for surface identification allow identification of the marked chemical changes at polymer surface after various pre-treatments.**
- **Surface analysis** refers to the characterization of the outermost layers of materials with a new series of **techniques based on ultra-high vacuum (UHV) technology,** that is important for two reasons:

(1) The material to be analysed is bombarded with particles (electrons or X-rays or ions or X-ray), and particles leaving the surface are detected (electrons or ions); these particles suffer collisions with residual gas molecules if the pressure is $>10^{-5}$ torr;

(2) Surfaces to be analysed can be rapidly contaminated by adsorption of residual gas molecules if the pressure is $> 10^{-5}$ torr.

Methods for polymer surface identification, *cont.*

- **Methods that provide information on surface chemical composition:**

- Auger electron spectroscopy (AES);
- X-ray photoelectron spectroscopy (XPS or ESCA);
- Secondary ion mass spectroscopy (SIMS);
- Ion scattering spectroscopy (ISS);
- Electron probe microanalysis (EPMA);
- Attenuated total internal reflection IR spectroscopy (ATR).

Chemical or elemental characterization of the surface and surface region of a solid provides direct information on its nature and of the bonding opportunities which it presents.

Methods for polymer surface identification, *cont.*

- **Comparison of some surface analysis techniques:**

Technique	Incident radiation	Emitted radiation	Depth analysed
AES	Electrons	Electrons	3 nm
XPS	X-ray	Electrons	3 nm
SIMS	Ions	Ions	2 mono-layers
ISS	Ions	Ions	outer atom layer
EPMA	Electrons	X-ray	1 µm
ATR	IR photons	IR photons	1 µm

Methods for polymer surface identification, *cont.*

Analysis of the surface region enables:

- Identification of possible bonding group;
- Identification of possible diffusion path;
- Analysis of local diffusion profiles;
- Identification of failure modes.

- **Surface analysis enables the determination of loci of failure in relation to:**

- Interface strength in composite materials;
- Adhesion of glues and coatings;
- Weak boundary layers and segregation in polymers.

Polymer adhesive materials

- **The term adhesive systems** is used for the **systems where the adhesion between the selected phases at the interface** and **its changes plays the crucial role in behaviour** of the system, besides the physical, chemical and other properties of the particular phases.
- For the **adhesion between polymers** (and plastics with additives) all mentioned **adhesion theories may have some role** depending on the particular adhesive system.
- **Polymer adhesive materials** under considerations:
- **Adhesives;**
- **Polymer blends;**
- **Polymer composites;**
- **Nanomaterials (e.g. nanoparticulate filled composites and/or blends)**.

Polymer adhesive materials, *cont.*

Adhesives

- **The primary purpose of an adhesives,** as a phase in adhesive joint, is **wetting and spreading** on the surface of a substrate, as another phase, and than **setting** by forming the **permanent and stable bonds at the interface**.
- **Adhesives** are **classified** in several ways, depending on the importance in application in a way:
- **How the adhesive and substrat will interact by adhesion** (e.g. solvent – based adhesives, emulsion and dispersion adhesives, hot melt adhesives, reaction setting adhesives, radiation cured adhesives, pressure-sensitive adhesives etc.);
- **By the chemical nature of adhesives** (e.g. epoxy adhesives, polyurethane adhesives, rubber-based adhesives etc.);
- **By the end use industry** (e.g. packing, automotive, aerospace, textile etc.).

Polymer adhesive materials, *cont.*

Polymer blends

- **In polymer blends** two or more **polymers** without, or with, other additives (e.g. nanofillers) are **mixed together.**
- **Polymers** are **usually incompatible and immiscible**, even if they are chemically very similar.

- The **conditions for compatibility**, that the Gibb's free energy for mixing (ΔG_m) is **negative** is **not commonly fulfilled when polymers are involved** (although the entropy term of mixing (ΔS_m), as a consequence of increased disorder is negative, the enthalpy term i.e. heat of mixing (ΔH_m) is often small and positive : $\Delta G_m = \Delta H_m - T\,\Delta S_m$.
- When **components in blend are incompatible** and immiscible this results in **weak interfacial interactions,** which limit their applications.
- **Interfacial energy, structure and adhesion at interface** are related to **the blend properties**.

Polymer adhesive materials, *cont.*

Polymer blends, *cont.*

- **The mixing of two polymers** will result in dispersion of one polymer in the matrix of another.
- **The polymer mixtures**, usually **immiscible**, form **multiphase structures with interfaces:**

\- The **dispersion, morphology, and adhesion of the component phases** and thus the **properties** are greatly **affected by the interfacial energies** i.e. by **surface and adhesion phenomena at the interface**.

\- **The function of the efficient compatibilizer** (e.g. copolymers, reactive mineral fillers etc.), **situated at the interface, with a role as dispersant, is to reduce the size of dispersed phase** and thus reduce the **morphology heterogeneity,** by **lowering the interfacial tension and allowing the strong mutual interactions to the phases.**

Polymer composites

- **Composite materials** consist of **two or more phases** with the **properties** that **depend not only on the properties of the individual phases** but also on the **adhesion between them at the interface** (e.g. high adhesion increases the mechanical strength, but lower adhesion may give greater fracture energy i.e. increases toughness etc.).
- **Science of adhesion is relevant in all multiphase adhesive systems** (composites, blends, adhesives, adhesive joints etc.) i.e. in the **materials with interfaces.**
- **By modifying or tailoring the interface** (e.g. by adding the surface modifiers such are adhesion promoters or by surface pre-treatments)**, the improved fundamental adhesion might result in the improved practical adhesion.**
- **The possibilities of 'engineering' the interface** in order to achieve the desired properties are **based on the understanding of the interface.**

Nanomaterials

Nanocomposites

- **Nanocomposites are multiphase materials** where at least one of the constituent phases has **one dimension less than 100 nm.**
- **Challenges** in investigations of nanocomposites:

- **Tailoring and understanding the role of interface** in creating the **unique combination of properties i.e. multi-functionality;**
- **Control over the distribution in size and dispersion of the nano-size constituents.**
- **Mother Nature** is we **should follow in creation** and controlled processing of nanomaterials **;** e.g. bone is built from ceramic tablets of hidroxy-apatite and organic protein binders, the structure of abalone shell is organic/inorganic layered nanocomposite etc).
- **Several interdisciplinary fields** are covered in **tailoring synthetic nanocomposites:** naturally inspired , based on inorganic materials, nanoparticle filled nanocomposites etc.

Nanocomposites, *cont.*

- **The interface controls the degree of interactions between filler and polymer and thus controls the properties**.

The interfaces in conventional material constitute a much **smaller volume fraction** of the bulk material than **in nanocomposites.**

Interfaces in nanocomposites between the constituent intermixed phases **is large,** compared to its microcomposite counterparts, due to the **high surface area of nanostructures.**

- It is important **to define and to control the interfacial region** in nanocomposites in order to achieve the controlled properties.

- **Interfacial region** can be a region of **altered chemistry, altered polymer chain mobility, altered degree of cure and altered crystallinity.**

Nano-particulate filled composites

- **Nanoscale filled polymer composites** – in which filler is < 100 nm in at least one dimension may **overcome the limitations of traditional micrometer-scale polymer composites.**

\- **The evenly distributed small size inorganic particles in polymer matrix:** do not scatter light significantly; do not create large stress concentration; create exceptionally large interfacial area (3D ‘interphase’); large amount of polymer matrix is under the influence of nanofillers.

- **Nanocomposites** offer **new properties** in comparison to the **conventional materials**.
- **Materials built from nanocomposites** can be **multifunctional** and **satisfy several functions at the same time** (e.g. increased strength and elasticity, increased stiffness and toughness, increased toughness and optical clarity, increased yield stress, the tensile strength and Young’s modulus etc.).

\- **Special properties of nanocomposite materials** arise from the **interactions at nano-levels** at the interface.

Nano-particulate filled composites, *cont.*

- **The interfacial area in nanocomposites** have the properties significantly different from those in the bulk:
- **If the interfacial region is more extended,** than the **polymer matrix behaviour** can be altered **at much smaller loadings** of nanofillers;
- The **increased polymer-particle interactions** result in a larger bound polymer fraction at the filler surface, that affect the nanocomposite properties.
- **In summary, the interfacial region is complex**, and when the interfacial region is very large, its affect the great amount of polymer matrix resulting in the unique properties of nanocomposites:
- It is important to develop the technology in order to **control nanoparticle dispersion and interface**;
- By **modifying the nanoparticle surface** it is **possible to change the interface and the properties** of the nanomaterial.

Optimal (effective) interface/interphase

Examples of investigations

Particulate filled composites and/or blends are heterogeneous systems where the

INTERFACE ◀ ▶ INTERFACE AREA ◀ ▶ INTERPHASE

▼

Seems to play a key role in determining the

PROPERTIES

▼

GOAL:

MICROCOMPOSITES ***vs*** NANOCOMPOSITES

IMMISCIBLE ***vs*** MISCIBLE BLENDS

MICROFILLERS ▶ Phase separation in composite ◀ NANOFILLERS

▼ ▼ ▼

MORPHOLOGY

Heterogeneous ◀ FILLER DISPERSION ▶ Homogeneous

▼ ▲

Negligible ◀ POLYMER MATRIX UNDER THE FILLER INFLUENCE ▶ Significant

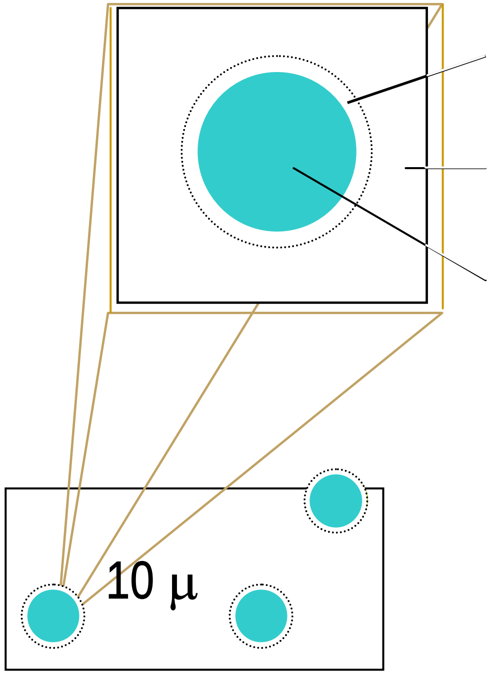
Optimal (effective) interface/interphase, *cont.*

Examples of investigations

PARTICULATE FILLED COMPOSITES:

Microcomposites *vs* nanocomposites

How we change the interphase by lowering the size of particles to nanodimensions ?



INTERFACIAL AREA (INTERPHASE) → **A KEY PLACE IN COMPOSITES, influences on PROPERTIES**

Polymer matrix

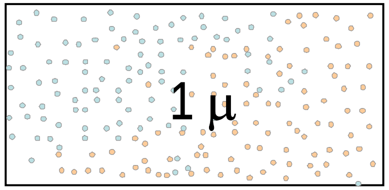
Filler

$$\boxed{B = (1 + l\,A_{\mathrm{f}}\gamma_{\mathrm{f}})\ln\frac{\sigma_{\mathrm{Ti}}}{\sigma_{\mathrm{To}}}}$$

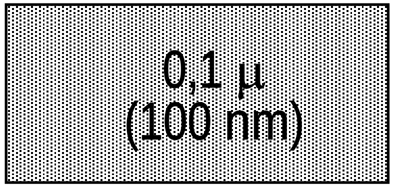
[1] B= coefficient of interactions
l= interphase thickness

3 vol % u 50.000 µm³

2,86 particles



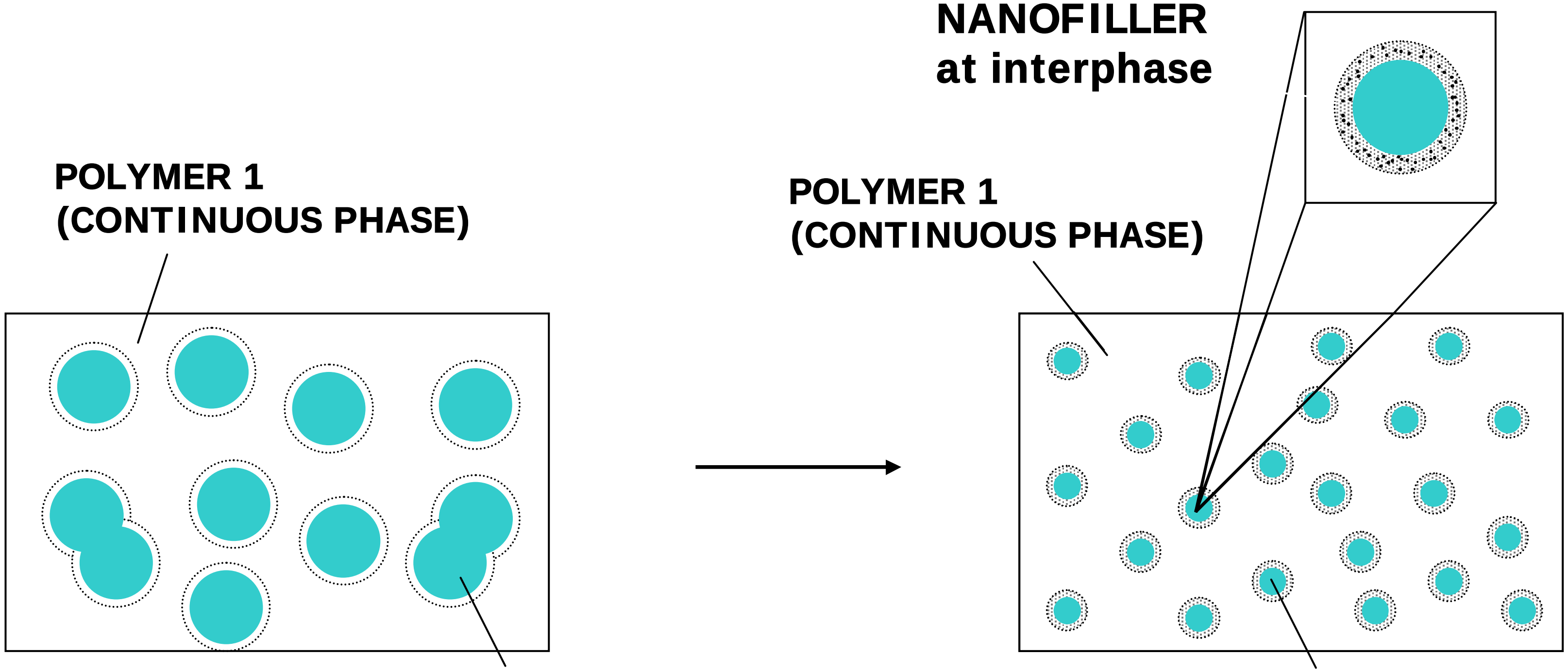
2.860 particles



2.86 · 10⁶ particles

Optimal (effective) interface/interphase, *cont.*

Examples of investigations, *cont.*



NANOFILLER
at interphase

POLYMER 1
(CONTINUOUS PHASE)

POLYMER 2
(DISPERSED PHASE)

LESS DISPERSED

COARSE MORPHOLOGY
HETEROGENEOUS

POLYMER 1
(CONTINUOUS PHASE)

POLYMER 2
(DISPERSED PHASE)

BETTER DISPERSED

FINER MORPHOLOGY
HOMOGENEOUS

Optimal (effective) interface/interphase, *cont.*

Examples of investigations, *cont.*

Fundamental Background:

Adhesion parameters at interface
between particulate fillers (f) and matrix (m):

WORK OF ADHESION

$$\boxed{W_{\mathrm{f/m}} = \gamma_{\mathrm{f}} + \gamma_{\mathrm{m}} - \gamma_{\mathrm{f/m}}}$$

Optimal-effective adhesion

MAXIMAL (optimal)

INTERFACIAL ENERGY

$$\boxed{\gamma_{\mathrm{f/m}} = \gamma_{\mathrm{f}} + \gamma_{\mathrm{m}} - \frac{4\gamma_{\mathrm{f}}^{\mathrm{d}}\gamma_{\mathrm{m}}^{\mathrm{d}}}{\gamma_{\mathrm{f}}^{\mathrm{d}} + \gamma_{\mathrm{m}}^{\mathrm{d}}} - \frac{4\gamma_{\mathrm{f}}^{\mathrm{p}}\gamma_{\mathrm{m}}^{\mathrm{p}}}{\gamma_{\mathrm{f}}^{\mathrm{p}} + \gamma_{\mathrm{m}}^{\mathrm{p}}}}$$

MINIMAL (≈ 0)

COEFFICIENT OF WETTING

$$\boxed{S_{\mathrm{f/m}} = \gamma_{\mathrm{f}} - \gamma_{\mathrm{m}} - \gamma_{\mathrm{f/m}}}$$

POSITIVE

Optimal (effective) interface/interphase, *cont.*

Examples of investigations, *cont.*

Conditions of effective adhesion at interface in

PARTICULATE FILLED BLENDS

between filler*(F) *and polymer matrices
***as continuous phase*(A) *and discontinuous phase*(B)**

Migration of filler: to interface

$$G^S_{AF} \geq G^S_{BF} - G_{AB}/2 \; ; \quad G^S_{BF} \geq G^S_{AF} - G^S_{AF}/2$$

$$(G^S_{AF} \approx G^S_{BF})$$

Wetting coefficient : $-1 > \omega a < 1$

$$\omega_a = \gamma_{F-B} - \gamma_{F-A} / \gamma_{A-B} \qquad \omega_a > 1 \text{ (F } in \text{ A) ; } \omega_a < -1 \text{ (F } in \text{ B)}$$

Spreading coefficient: $\lambda_{A-C} \rightarrow 0$

$$\lambda_{A-F} = \gamma_{B-F} - \gamma_{A-B} - \gamma_{A-F}$$

$$\lambda_{A-F} > 0 \text{ (F } in \text{ B) ; } \lambda_{A-F} < 0 \text{ (F } in \text{ A)}$$

Optimal (effective) interface/interphase, *cont.*

Examples of investigations, *cont.*

THE ACHIEVEMENTS OF THE CONDITIONS OF OPTIMAL 'EFFECTIVE' ADHESION AT THE INTERFACE IS EXPECTED TO RESULTS IN SIGNIFICANT IMPROVEMENT OF PROPERTIES IN NANOPARTICULATE FILLED COMPOSITES, BLENDS AND RELATED PRODUCTS.

THE SELECTED NANOFILLER SURFACE PRE-TREATMENT MIGHT RESULT IN IMPROVEMENTS OF ADHESION AT THE INTERFACE AND IN SIGNIFICANT PROPERTIES IMPROVEMENTS OF THE PARTICULATE FILLED MATERIALS AND PRODUCTS AS A WHOLE.

Conclusion

- **By knowing the surface and interface phenomenon in polymer multiphase systems one should be able to control the interface/interphase region and in this way to control the properties, in order to get the new generation of advanced generic materials with multifunctionality in properties.**

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