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MATERIALS PROCESS ENGINEERING

INPACT OF FILLERS ON GAS PERMSELECIVITY OF MIXED MATRIX MEMBRANES

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AMIRA MECHENTEL

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الملخص

قمنا في هذا العمل بجمع بيانات النفاذية من 38 أغشية مصفوفة مختلطة ودرسنا أداءها لفصل الأنظمة الغازية CO_2 / N_2و CO_2 / CH_4. لتحليل هذه البيانات ، استخدمنا النطاق العلوي ل Robeson وقارنا أداء بوليمرات المصفوفة وغشاء المصفوفة المختلطة على مستويات مختلفة من الحشوات المختلفة. يؤدي إدخال مواد الحشوات مثل الزيوليت والسيليكات والأنابيب النانوية الكربونية والكربون إلى تعديل الارتباطات الكيميائية لمنافذ الاختراق في الغشاء النانوي المركب مما يؤدي في معظم الحالات إلى زيادة النفاذية مع انخفاض طفيف في الانتقائية. لاحظنا، في بعض الحالات، عدم وجود أي تأثير، في حالات أخرى ، زيادة قوية في النفاذية لا غير. تؤدي إضافة حشو نوع MOFs فقط إلى زيادة ملحوظة في كل من الانتقائية والنفاذية في وقت واحد.

Abstract

In this work, we collected permeability data from 38 Mixed Matrix Membranes and studied their permselectivity performance for the separation of CO_2 / N_2 and CO_2 / CH_4 gaseous systems. To analyze this data, we used Robeson's upper band and compare the performance of the matrix polymers and their Mixed Matrix Membranes at different levels of different fillers. The introduction of fillers such as zeolites, silicates, carbon and carbon nanotubes, modifies the chemical affinities of the penetrants in the nanocomposite membrane which leads, in the majority of cases, to an increase in the permeability with a slight decrease in selectivity. We observed, in some cases, no effect, in other cases, only a strong increase in permeability. Only the addition of MOFs type filler leads to a remarkable increase in both the selectivity and the permeability simultaneously.

Résumé

Dans ce travail, nous avons collecté des données de perméabilité de 38 Mixed Matrix Membrane et étudié leurs performances en permselectivité pour la séparation des systèmes gzeux CO_2 / N_2 et CO_2 / CH_4. Pour analyser ces données, nous avons utilisé la bande supérieure de Robeson et comparer les performances de la matrice des polymères et de leurs Mixed Matrix Membrane à différentes teneurs en différente matières de charge. L'introduction de matières de charge tel que les zéolites, les silicates, le charbon et les nanotubes de carbone, modifie les affinités chimiques des pénétrations dans la membrane nanocomposite ce qui conduit, dans la majorité des cas, à une augmentation de la perméabilité avec une légère diminution de la sélectivité. Nous avons observé, dans certains cas, aucun effet, dans d'autres cas, une forte augmentation de la perméabilité uniquement. Seul l'ajout de charge de type MOFs conduit à une augmentation remarquable à la fois de la sélectivité et de la perméabilité simultanément.

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GENERAL INTRODUCTION

MMM has been the subject of worldwide academic studies conducted by many researchers especially those related to membrane technology. The past decades have witnessed substantial progress and exciting breakthroughs in both the fundamental and application aspects of MMM in various forms of separation, particularly in gas separation.

These emerging materials for separation have been traditionally accomplished by incorporating conventional inorganic fillers such as zeolite, carbon molecular sieve and silica nanoparticles in a polymer matrix. The recent advances have shifted towards the introduction of new and novel materials namely carbon nanotubes, metal organic framework and clay layered silicate as potential fillers in the polymer matrix.

The successful implementation of MMM depends greatly on the polymer matrix selection, the inorganic filler as well as the interaction between the two phases. The selection of suitable types of inorganic filler, the surface modification, and the performance of the resulted MMM membranes were keys of success.

The recent efforts to tackle the underlying problems and the effects of various kinds of modifications that would eventually heighten the performance of membrane applications in gas separations were discussed. Better understanding on the improvement and optimization of MMM process was provided by considering the possible solutions to overcome the problems encountered during MMM preparation.

This study consists of enriching the existing database on polymers available in Materials and Environmental Laboratory of Médéa University with MMMs used in gas separation, mainly those used in the separation of CO_2 /N_2 system and CO_2/CH_4 system with recently published new materials and examen their gas permeability by exploiting the relationship between microstructure of these materials and the property of permeability to gas.

This work consists of two parts:

The first part is a bibliographical summary made up of four points

- A general overview of polymers: definition, classification, application polymers, their synthesis methods, polymerization techniques industrial and at the end of this part an overview on polymers inorganic.

- The second point is a general representation on hybrid materials based on their definition, classification, production processes and ultimately their applications.
- The third point is a bibliographical study on mixed matrix membranes, the definition, families of MMMs, the characteristics, the methods of synthesis and finally their applications.
- This point is reserved for the study of perm selectivity mixed matrix membranes, the different laws that manage permeability and ultimately the parameters influencing the permeability of gases in membrane films.

The second part is the collection of gas permselectivities data from publications, their homogenization and their analysis. It includes discussion and interpretation of trends of permselectivity function of matrix type and fillers.

At the end of this work a general conclusion was drawn up to summarize the results extracted this work.

I. GENERALITY ON POLYMERS

I.1 Concepts and nomenclature

The origins of polymer science and the polymer industry have existed in the natural form since life began, and those such as DNA , RNA, proteins and polysaccharides play crucial roles in plant and animal life. From the earliest times, man has exploited naturally-occurring polymers as materials for providing clothing. Decoration, shelter, tools, weapons, writing materials and other requirements. However, the origins of today‘s polymers industry commonly are accepted as being in the nineteenth century when important discoveries were made concerning the modification of certain natural polymers.[1]

The word “polymer” was introduced by the Swedish chemist J. J. Berzelius. He considered, for example, benzene (C_6H_6) to be a polymer of ethyne (C_2H_2). Later this definition underwent a subtle modification

In the 1820. Thomas Hancock discovered that when masticated (Natural rubber becomes more fluid making it easier to blend with additives and to mould. Some years later, in1839. Charles Goodyear found that the elastic properties of natural rubber could be improved, and its tackiness eliminated, by heating with sulphur. Parents for this discovery were issued in 1844 to Goodyear, and slightly earlier to Hancock, how christened the process vulcanization. In 1851, Nelson Goodyear, Charles` brother, ebonite or vulcanite.[2]

Cellulose nitrate, nitrocellulose or gun cotton, first become prominent after Christian Schonbien prepared it in 1846. Alexander Parkes was the first to take advantage of this combination of properties and in 1862 . In 1870, John and Isaiah Hyatt parented a similar but more easily processed material, named celluloid.

In 1892, Charles Cross, Edward Bevan and Clayton Beadle parented the viscose process for dissolving and then regenerating cellulose. Leo Baekeland’s phenol-formaldehyde `Bakelite` resins have the distinction of being the fully synthetic polymers to be commercialized, their production beginning in 1910.

Scientists had been reporting the unusual properties of polymers, and by 1920[3], . Staudinger introduced the word `macromolecule` to describe polymers, and during the 1920s. . Thus by the early 1930s, most scientists were convinced of the macromolecular structure of polymers. During the following 20 years, work on polymers increased enormously. The theoretical and experimental work on Paul Flory was prominent in this period, and for his long and substantial contribution to polymer science, he was awarded the Nobel Prize for Chemistry in 1974. In 1953, Staudinger had received the same accolade in recognition of his pioneering work.

. These include polystyrene, poly (methyl methacrylate), nylon 6.6, polyethylene, poly(vinyl chloride), styrene-butadiene rubber, silicon and polytetrafluroethylene, as well as many others. From the 1950s .

I.2 Basic definitions and nomenclature

Several important terms and concepts must be understood in order to discuss fully the synthesis, characterized, structure and properties of polymers. .

In strict terms, a polymer is a substance composed of molecules which have long sequences of one or more species of atoms or groups of atoms linked to each other by primary,

Macromolecules are formed by linking together monomer molecules through chemical reactions, the process by which this is achieved being known as polymerization.

I.2.1 Structure

The definition of macromolecules presented up to this point implies that they have a linear structure which may be represented by a chain with two ends. Whilst this is true for many macromolecules, there are also many with non-linear structures of the type show in.[4]

Cyclic polymers (ring polymers) have no chain ends and show properties that are quite different to their counterparts. Branched polymers have side chains, or branches, of significant length which are bonded to the main chain at branch points. Network polymers have three-dimensional structures in which each chain is connected to all others by a sequence of junction points and others chains.

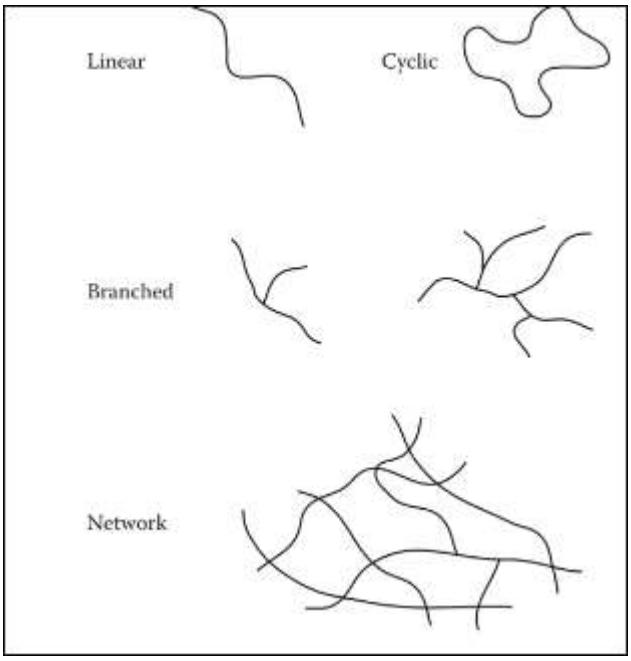


Figure I-1 structures representative of linear, cyclic and non-linear polymers.

These variations in structure give rise to major differences in properties. Unlike linear and branched polymers, network polymers do not melt upon heating and will not dissolve, though they may swell considerably in compatible solvents. The importance of crosslink density has already been described in terms of the vulcanization of natural rubber. With low crosslink densities the product is a flexible *elastomer*, whereas it is a rigid material when the crosslink density is high as shown in Figure I-2.

In addition to these more conventional structures, there has been a growing interest in more elaborate skeletal forms of macromolecules.

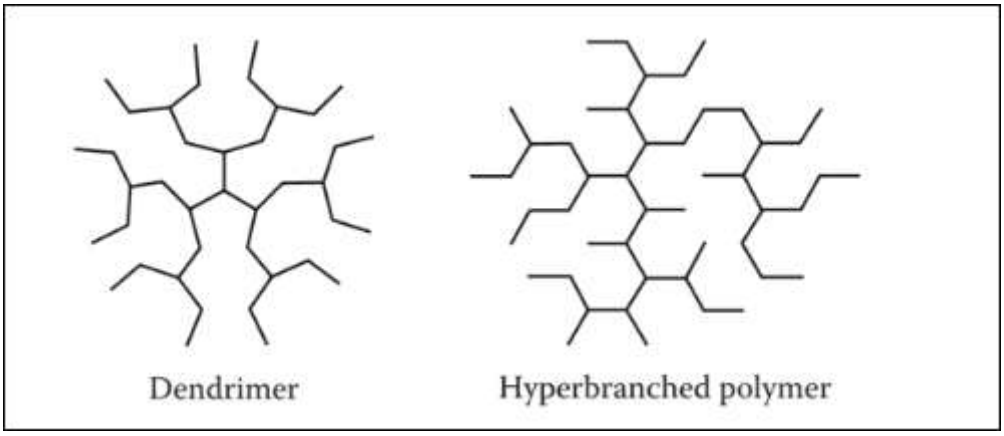


Figure I-2 skeletal structures representative of dendrimers and hyperbranched polymers homopolymers

The formal definition of $the\ homopolymer$ is a polymer derived from one species of monomer. However, the word $homopolymer$ often is used more broadly to describe polymers whose structure can be represented by multiple repetition of repeat units which may contain one or more species of monomer unit. The latter is sometimes referred to as a structure unit. As shown in Table I-1.

The chemical structure of a polymer is usually represented by a repeat unit enclosed by brackets. Thus the hypothetical homopolymer :

~A-A-A-A-A-A-A-AA-A-A~ is represented by$-[A]n-$ where n is number of some repeat units linked together to form the macromolecule. table 1.1 show the chemical structures of some common homopolymers together with the monomers from which they are derived and some comments upon their properties and uses.

Table I-1 Some Common Homopolymers.

Monomer	polymer	Comment
1. Ethylene CH2═CH2	Polyethylene (PE) *n*	Moulded objects, tubing, film, electrical insulation, e.g. ‘Alkathene’, ‘Lupolen’.
2. Propylene	Polypropylene (PP) *n*	Similar uses to PE; lower density, stiffer, e.g. ‘Propathene’, ‘Novolen’.
3. Tetrafluoroethylene	Polytetrafluoroethylene (PTFE)*n*	Mouldings, film, coatings; high temperature resistance, chemically inert, excellent electrical insulator, very low coefficient of friction; expensive, e.g. ‘Teflon’, ‘Fluon’.
4. Styrene	Polystyrene (PS) *n*	Cheap moulded objects, e.g. ‘Styron’, ‘Hostyren’. Modified with rubbers to improve toughness, e.g. high-impact polystyrene (HIPS) and acrylonitrile–butadiene–styrene copolymer (ABS). Expanded by volatilization of a blended blowing agent (e.g. pentane) to produce polystyrene foam.
5. Methyl methacrylate	Poly(methyl methacrylate) (PMMA) *n*	Transparent sheets and mouldings; used for aeroplane windows; more expensive than PS, e.g. ‘Perspex’, ‘Diakon’, ‘Lucite’, ‘Oroglass’, ‘Plexiglas.
6. Vinyl chloride	Poly(vinyl chloride) (PVC) *n*	Water pipes and gutters, bottles, gramophone records; plasticized to make PVC leathercloth, raincoats, flexible pipe and hose, toys, sheathing on electrical cables, e.g. ‘Darvic’, ‘Welvic’, ‘Vinoflex’, ‘Hostalit’.

7. Vinyl acetate	Poly(vinyl acetate)n	Surface coatings, adhesives, chewing gum
8. Ethylene oxide	Poly(ethylene oxide) (PEO)n	Water-soluble packaging films, textile sizes, thickeners, e.g. 'Carbowax'
9. Ethylene glycol and terephthalic acid	Poly(ethylene terephthalate) (PET)	Textile fibres, film, bottles, e.g. 'Terylene', 'Dacron', 'Melinex', 'Mylar'
10. Hexamethylene diamine and sebacic acid	Poly(hexamethylene sebacamide) (nylon 6.10)	Mouldings, fibres, e.g. 'Ultramid 6.10.

I.2.2 Copolymers

The formal definition of a *copolymer* is a polymer derived from more than one species of monomer. Thus the word copolymer more commonly is used to describe polymers whose molecules contain two or more different types of repeat unit. Hence polymers (9) and (10) in table 1.1 are usually considered to be homopolymers rather than copolymers.

the representation of these categories will be illustrated by copolymers containing only two different types of repeat unit (A and B). A section of a truly random copolymer is represented below.

~B-B-B-A-A-A-A-AB-B-B~.

Alternating copolymers have only two different types of repeat units and these are arrangement alternately along the polymer chain

~A-B-A-B-A-B-A-B-A-B~.

Block copolymers are linear copolymers in which the repeat units exist only in long sequences, or *blocks*, of the same type. Two common block copolymer structures are represented below and are usually termed AB di-block and ABA tri-block copolymers, Only one structure the first [A]n[B]m.

~A-A-A-A-A-A-B-B-B-B-B-B-B-A-A-A-A-A-A-A-A~

Graft copolymers are branched polymers in which the branches have a different chemical structure to that of the main chain. In their simplest different homopolymer, comb-like copolymer like it shown in(Figure I-3)

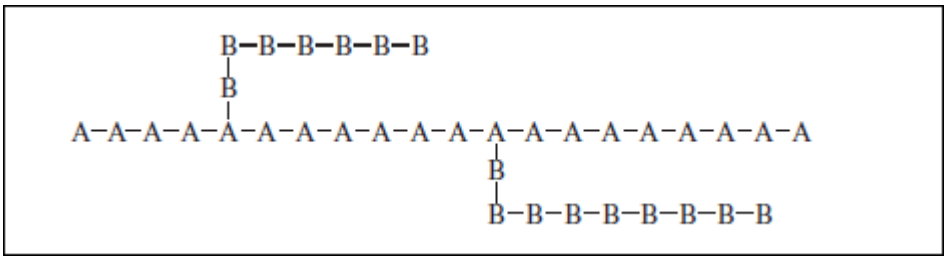


Figure I-3 Grafted copolymer

I.2.3 Classification of polymers

First of all describe the different principles of classifying before using one them The most common way of classifying polymers is outlined in the (Figure I-4) where they are first separated into three groups: *thermoplastics, elastomers and thermosets*.

Thermoplastics are further separated into those which are crystalline and those which are amorphous (i.e. non-crystalline). This method of classification has an advantage in comparison to others since it is based essentially upon the underlying molecular structure of the polymers[5].

Thermoplastics, often referred to just as plastics, are linear or branched polymers which become liquid upon the application of heat. They can be moulded (and remoulded) into virtually any shape using processing techniques such as injection moulding and extrusion, and now constitute by far the largest proportion to the polymers in commercial production. Generally, thermoplastics do not crystallize easily upon cooling to solid state because this requires considerable ordering of the highly coiled and entangled macromolecules present in the liquid state. , they are intractable once formed and degrade rather than become fluid upon the application of heat. Hence, their processing into artifacts is often done using processes, such as compression moulding, that require minimum amounts of flow[6].

Table I-2 Principles of nomenclature for copolymers.

Type of Copolymer	Example of Nomenclature
Unspecified	Poly(A-*co*-B)
Statistical	Poly(A-*stat*-B)
Random	Poly(A-*ran*-B)
Alternating	Poly(A-*alt*-B)
Block	PolyA-*block*-polyB
Grafta	PolyA-*graft*-polyB

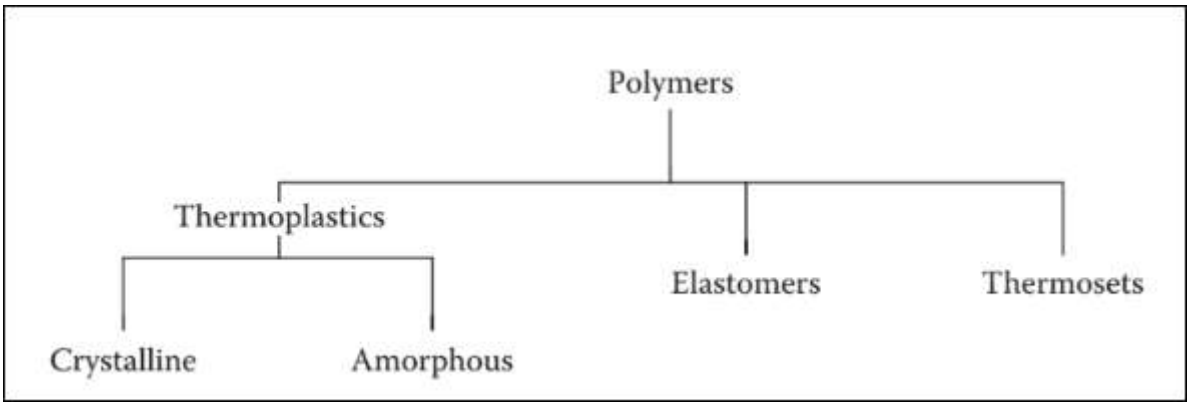


Figure I-4 classification of polymers.

I.3 Molar mass and degree of plymerization

Many properties of polymers show a strong dependence upon the size of the polymer chains, so it is essential to characterize their dimensions. This is normally done by measuring the molar mass M of a polymer

For network polymers the only meaningful molar mass is the polymer chains existing between junction points (i.e.$network\ chains$). Since the molar mass of the network itself essentially is infinite.

The molar mass of a homopolymer is related to the $degree\ of\ polymerization\ x$, which is the number of repeat units in the polymer chain, by the simple relation

$$M = xM_0 \qquad (1.1)$$

Where M_0 is the molar mass of the repeat unit. Equation 1.1 can also be used for copolymers, but M_0 needs to be replaced by M_0^{cop}, which is the mean repeat unit molar mass of the copolymer taking into account its composition

$$M^{cop}_{=\sum x_j M_0^j} \qquad (1.2)$$

Where

x_j Is the mole fraction, and

M_0^j the molar mass of repeat units of type ‘j’ in the copolymer.

I.3.1 Molar mass distribution

With very few exceptions, polymers consist of macromolecules (or network chains) with a range of molar masses. Since the molar mass changes in intervals of M_0, the distribution of molar mass is discontinuous. However, for most polymers, these intervals are extremely small in comparison to the total range of molar mass and the distribution can be assumed to be continuous, as exemplified in figure 1.4.

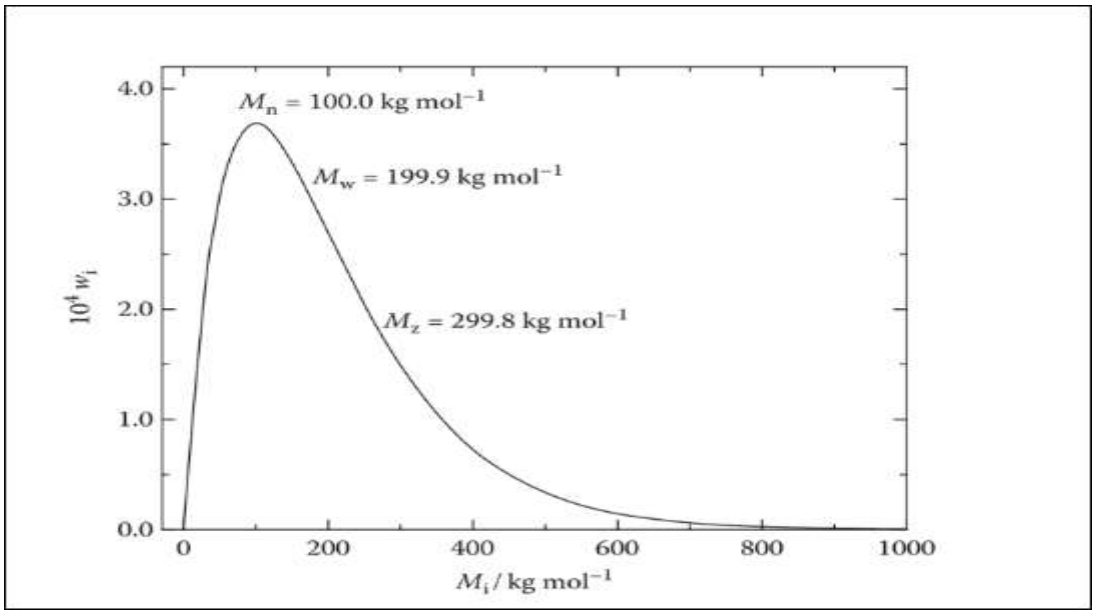


Figure I-5 A typical weight-fraction molar mass distribution curve (for a polymer with the most probable distribution of molar mass and a repeat unit molar mass of $100 gmol^{-1}$).

1.3.2 Molar mass averages

Whilst a knowledge of the complete molar mass distribution is essential in many uses of polymers, it is convenient to characterize the discontinuous nature of the distribution in terms of molar mass averages. These are usually defined by considering the discontinuous nature of the distribution in which the macromolecules exist in discrete fractions 'i' containing N_i molecules of molar mass M_i.

The $number - average\ molar\ mass \bar{M}_n$ is defined as the sum of the products of each fraction multiplied by its mole fraction, i.e.

$$\bar{M} = \sum X_i M_i \qquad (1.3)$$

Where X_i is the mole fraction of molecules of molar mass M_i and given by the ratio of N_i to the total number of molecules.

$$\overline{M_n} = \frac{\sum N_i M_i}{\sum N_i} \qquad (1.4)$$

Therefore it follows that showing this average to be the arithmetic mean of the molar mass distribution. It is often more convenient to use weight fractions rather than a number of molecules. The weight fraction W_i is defined as the mass of molecules of molar mass M_i divided by the total mass of all the molecules present, i.e.

$$W_i = \frac{N_i M_i}{\sum N_i M_i} \qquad (1.5)$$

From which it can be deduced that

$$\sum\left(\frac{W_i}{M_i}\right) = \frac{\sum N_i}{\sum N_i M_i} \qquad (1.6)$$

Combining equations 1.4 and 1.6 give $\overline{M_i}$ in terms of weight fractions

$$\overline{M_i} = \frac{1}{\sum(W_i/M_i)} \qquad (1.7)$$

The weight-average molar mass $\bar{M}_W$ is defined as the sum of the products of the molar mass of each fraction multiplied by its weight fraction, i.e.

$$\bar{M}_w = \sum w_i\, M_i \qquad (1.8)$$

By combining this equation 1.5, $\bar{M}_W$ can be expressed in terms of the numbers of molecules

$$\bar{M}_w = \frac{\sum N_i\, M_i^2}{N_i M_i} \qquad (1.9)$$

The ratio $\bar{M}_w/\bar{M}_n$ must by definition be greater than unity for a $polydisperse$ polymer and is known as the $polydispersity$ or $heterogenety\ index$ (often referred to as PDI). Its value is often used as a measure of the breadth of the molar mass distribution, though it is a poor substitute for knowledge of the complete distribution curve. Typically $\bar{M}_w/\bar{M}_n$ is in the range 1.5-2.0, though there are many polymers which have smaller or very much larger value of polydispersity index. A perfectly $monodisperse$ polymer would have $\bar{M}_w/\bar{M}_n = 1.00$.

Higher molar mass average than $\bar{M}_w$ sometimes are quoted. For example, certain methods of molar mass measurement (e.g. sedimentation equilibrium and dynamic light scattering) yield the $z-average\ molar\ mass\ \bar{M}_z$, which is defined as follows

$$\bar{M}_z = \frac{\sum \mathrm{N_i M_i^3}}{\sum N_\mathrm{i} \mathrm{M_i^2}} = \frac{\sum W_\mathrm{i} \mathrm{M_i^2}}{\sum W_\mathrm{i} \mathrm{M}_i} \qquad (1.10)$$

In addition, averages with more complex exponents are obtained from other methods of polymer characterization (e.g. from dilute solution viscometry and sedimentation measurements).

Degree of polymerization averages are of more importance than molar mass averages in the theoretical treatment of polymers and polymerization, as will be highlighted in the subsequent chapters. For homopolymers they may be obtained simply by dividing the corresponding molar mass average by M_0. Thus the $number-average$ and $weight-average\ degrees\ of\ polymerization$ are given by

$$\bar{x}_n = \frac{\bar{M}_n}{\bar{M}_0} \qquad (1.11)$$

And

$$\bar{x}_w = \frac{\bar{M}_w}{\bar{M}_0} \qquad (1.12)$$

The same equations can be applied to calculate $\bar{x}_n$ and $\bar{x}_w$ for copolymers by replacing $\bar{M}_0$ with $\bar{M}^{COP}$.

I.4 Principles of polymerization

The most basic requirement for polymerization is that each molecule of monomers must be capable of being linked to two (or more) other molecules of monomers by chemical reaction, i.e. monomers must have a $functionality$ of two (or higher). Given this relatively simple requirement, there are a multitude of chemical reactions and associated monomer types that can be used to effect polymerization.

Consequently, the number of different synthetic polymers that have been prepared is extremely large and many can be formed by more than one type of polymerization. Hence, the number of individually different synthetic polymers that have been prepared is extraordinarily large. To discuss each of these would be an enormous task which fortunately is not necessary since it is possible to categorize most polymerization reactions into a relatively small number of classes of polymerization, each class having distinctive characteristics[7].

I.5 Classification of polymerization reactions

The classification of polymerization reactions used in the formative years of polymer science was due to Carothers and is based upon comparison of the molecular formula of a polymer with that of the monomer(s) from which it was formed. $condensation\ polymerizations$ are those which yield polymers with repeat units having fewer atoms than are present in the monomers from which they are formed. This usually arises from chemical reactions which involve the elimination of a small molecule (e.g. H_2O, HCl). $addition\ polymerizations$ are those which yield polymers with repeat units having identical molecular formulae to those of monomers from which they are formed. Table 1.1 contain examples of each class of polymerization reactions : the latter two examples condensation polymerizations involving elimination of H_2O, whereas the others are addition polymerizations.

Carothers' method of classification was found to be unsatisfactory when it was recognized that certain condensation polymerizations have features characteristic of typical condensation polymerizations. A better basis for classification is provided by considering the underlying polymerization mechanisms, of which there are two general types. Polymerizations in which the polymer chains grow step-wise by reactions that can occur between any two molecular species are known as $step-growth\ polymerizations$. polymerizations in which a polymer chain grows only by reaction of monomers with a reactive end-group on the growing chain are known as $chain-growth\ polymerizations$, and usually require an initial reaction between the monomer and an $initiator$ to the start the growth of the chain.

modern preference is to simplify these manes to $step\ polymerization$ and $chain\ polymerization$, and this practice will be used here. The essential differences between these classes of polymerization are highlighted in Table I-3 which illustrates for each mechanism the reactions involved in growth of the polymer chains to a degree of polymerizations to a degree of polymerizations equal to eight. In step polymerizations the degree of polymerization increases steadily throughout the reaction, but the monomer is rapidly consumed in its early stages (e.g. when $\bar{x}_n = 10$only 1% of the monomer remains unreacted).

All the polymer chains continue to grow throughout the reaction as the conversion of functional groups into chain links increases. Carothers was quick to recognize that in order to attain even moderately high degrees of polymerization ($\bar{x}_n > 100$). By contrast, in chain polymerizations, high degree of polymerization are attained at low monomer conversions, the monomer being consumed steadily throughout the reaction.

TABLE I-3 Schematic illustration of the fundamental differences in reaction mechanism between step polymerization and chain polymerization

Formation of	**Step Polymerization**	**Chain Polymerization**
Dimer	o + o → o–o	I + o → I–o I–o + o → I–o–o
Trimer	o–o + o → o–o–o	I–o–o + o → I–o–o–o
Tetramer	o–o–o + o → o–o–o–o	I–o–o–o + o → I–o–o–o–o
Pentamer	o–o + o–o → o–o–o–o o–o–o–o + o → o–o–o–o–o	I–o–o–o–o + o → I–o–o–o–o–o
Hexamer	o–o–o–o–o + o → o–o–o–o–o–o o–o + o–o–o–o → o–o–o–o–o–o o–o–o + o–o–o → o–o–o–o–o–o	I–o–o–o–o–o + o → I–o–o–o–o–o–o
Heptamer	o–o–o–o–o–o + o → o–o–o–o–o–o–o o–o + o–o–o–o–o → o–o–o–o–o–o–o o–o–o + o–o–o–o → o–o–o–o–o–o–o	I–o–o–o–o–o–o + o → I–o–o–o–o–o–o–o
Octomer	o–o–o–o–o–o–o + o → o–o–o–o–o–o–o–o o–o + o–o–o–o–o–o → o–o–o–o–o–o–o–o o–o–o + o–o–o–o–o → o–o–o–o–o–o–o–o o–o–o–o + o–o–o–o → o–o–o–o–o–o–o–o	I–o–o–o–o–o–o–o + o → I–o–o–o–o–o–o–o–o

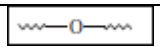
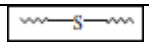
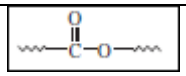
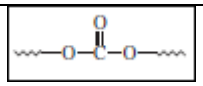
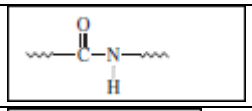
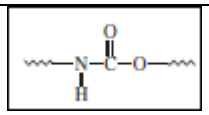
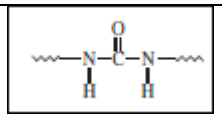
I = initiator species, o = molecule of monomer and repeat unit, – = chemical link.

I.6 Monomer functionality and polymer structure

The $functionality$ of a monomer is best defined as the number of chain links it can give rise to, because it is not necessarily equal to the number of functional groups present in the monomer. The first seven examples in Table I-4 are of polymers formed by chain polymerizations of olefinic monomers which contain a single C=C double bond; these monomers have a

functionality of two because each C=C double bond gives rise to two chain links. If a monomer has a functionality greater than two, then this will lead to the formation of branches and possibly to the formation of a network polymer, depending on the particular polymerization and reactant stoichiometry.

Table I-4 Some common classes of polymer named according linking grop in the chain backbone

Class of Polymer	Structure of Linking Group
Polyether	
Polysulphide	
Polyester	
Polycarbonate	
Polyamide	
Polyurethane	
Polyurea	

The effect of monomer functionality is illustrated schematically in Figure I-6The formation of dendrimers and hyperbranched polymers is achieved using monomers with functionalities of three or higher, but in a way that controlled so that a network polymer cannot form.

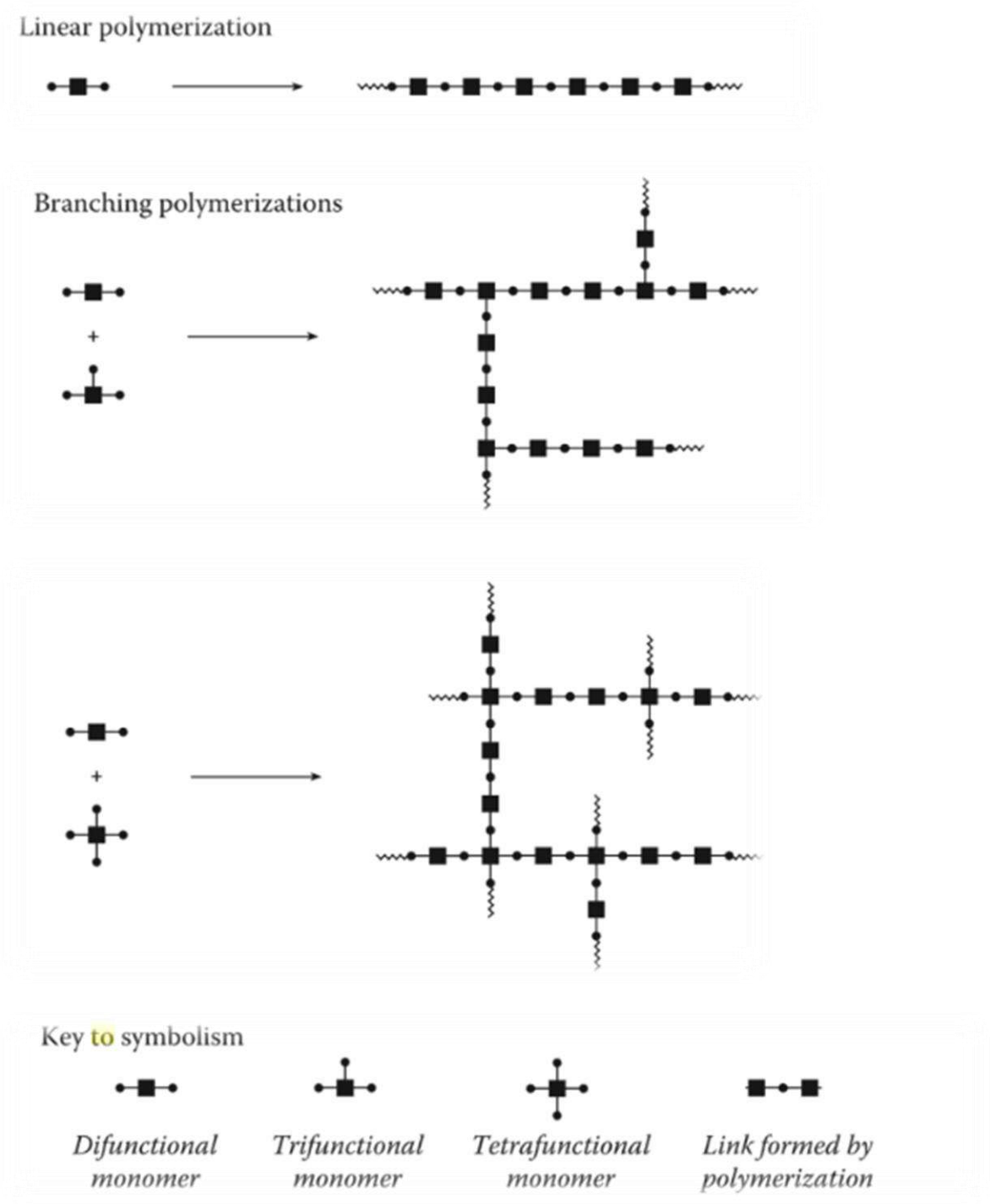


Figure I-6 schematic representations of how polymer structure is affected by monomer functionality

I.7 Step polymerization

Step polymerizations are, in most cases, logical extensions of simple organic chemistry linking reactions to chain formation and were the first types of polymerizations to be understood from a fundamental perspective, the work of Carothers during the 1920s and 1930s being seminal in this respect.

Most step polymerizations involved reactions which produce links that contain a heteroatom and so the polymers normally are grouped into generic classes according to the type of links created in the polymerization. Some of the most common classes of polymers named according to the linking group in the chain backbone.

The majority of step polymerizations are based on quite simple linking reactions and, for linear step polymerizations; the greatest challenge is the need to take the reactions to extremely high conversions in order to produce chains of sufficient length to realize useful properties. This is very demanding and, as a consequence, most polymers produced by linear step polymerizations have molar masses in the range 10-100$Kgmol^{-1}$, but more often 15-30 $Kgmol^{-1}$, which is much lower than for polymers prepared by chain polymerizations (typically 50-10,000 $Kgmol^{-1}$)

I.7.1 Step polymerization

Step polymerizations involve successive reactions between pairs of mutually-reactive functional groups which initially are provided by the monomer(s). The number of functional groups present on a molecule of monomer is crucial importance, as can be appreciated by considering the formation of ester linkages from the condensation reaction of carboxylic acid groups with hydroxyl groups. Acetic acid and ethyl alcohol are $monofunctional$ compounds which upon reaction together yield ethyl acetate with elimination of water

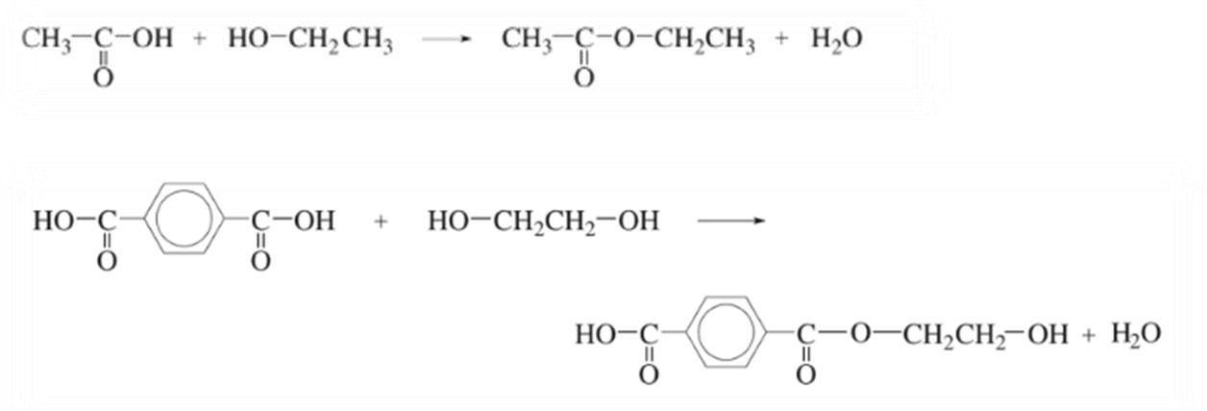


Figure I-7 polycondensation reaction

But because ethyl acetate is incapable of futher reaction, a polymer chain cannot form.now consider the reaction between terephthalic acid and ethylene glycol, both of which are $difunctional$

I.7.2 Polymerization in stages (POLYCONDENSATION)

The formation of molecules by this method is done initially from di- or multifunctional monomers according to the classic reactions of organic chemistry: esterification, nucleophilic substitution…. Then the chains continue to lengthen by the same reactions between functional groups carried by the monomer molecules and by the macromolecules in formation [8].

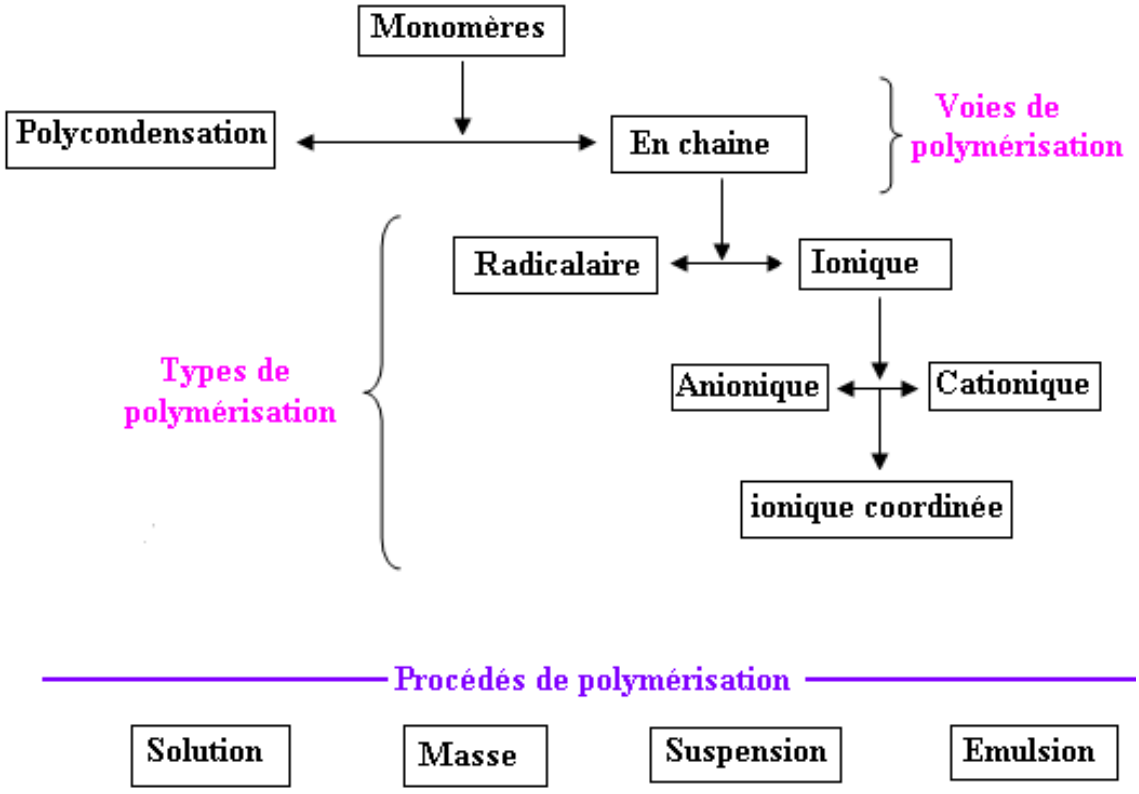


Figure I-8 Diagram of different polymerization routes

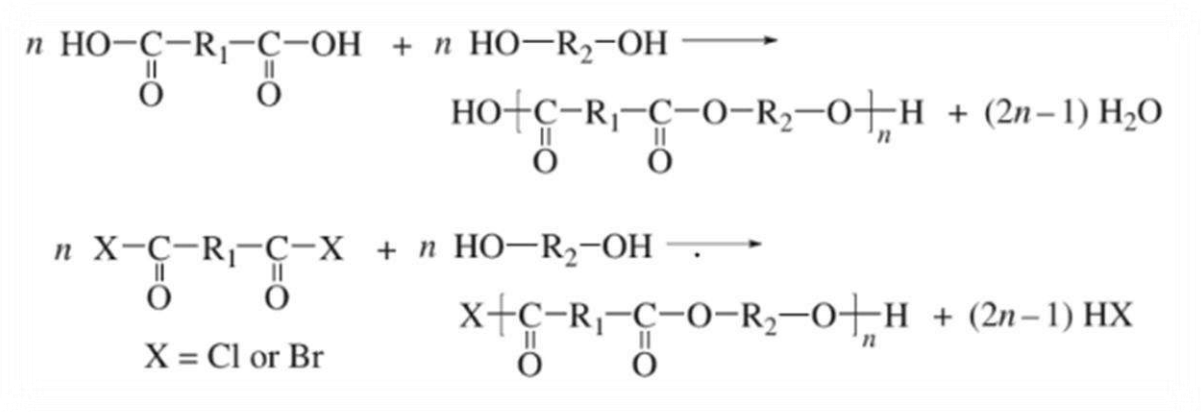


Figure I-9 Polyester synthesis from.

Where R_1 and R_2 represent any divalent group (usually hydrocarbon). Reaction between carboxylic acid and alcohol groups is slow and the reactions have to be performed at moderate-to-

high temperatures (80-300℃), usually in the presence of an acid catalyst. The reaction between terephthenic acid and ethylene glycol show in section 2.4 produces poly (ethylene terephthalate), the most widely used polyester. Carboxylic acid halides are much more reactive and their reactions with alcohol groups to produce polyesters proceed at room temperature, so they are used in simple laboratory syntheses of polyesters.

Reactions of the type shown above are referred to as $RA_2 + RB_2$ *step polymerizations* where R is any divalent group and A and B represent the mutually-reactive functional groups.

Polyesters also can be prepared from single monomers which contain both types of functional group, i.e. ω-hydroxy carboxylic acids

With each condensation reaction, the polymer chain grows but remains an ω-hydroxy carboxylic acids and so can react further.

Polyamides can be prepared by polycondensations analogous to those used to prepare polyesters, the hydroxyl groups simply being replaced by amine groups, e.g.

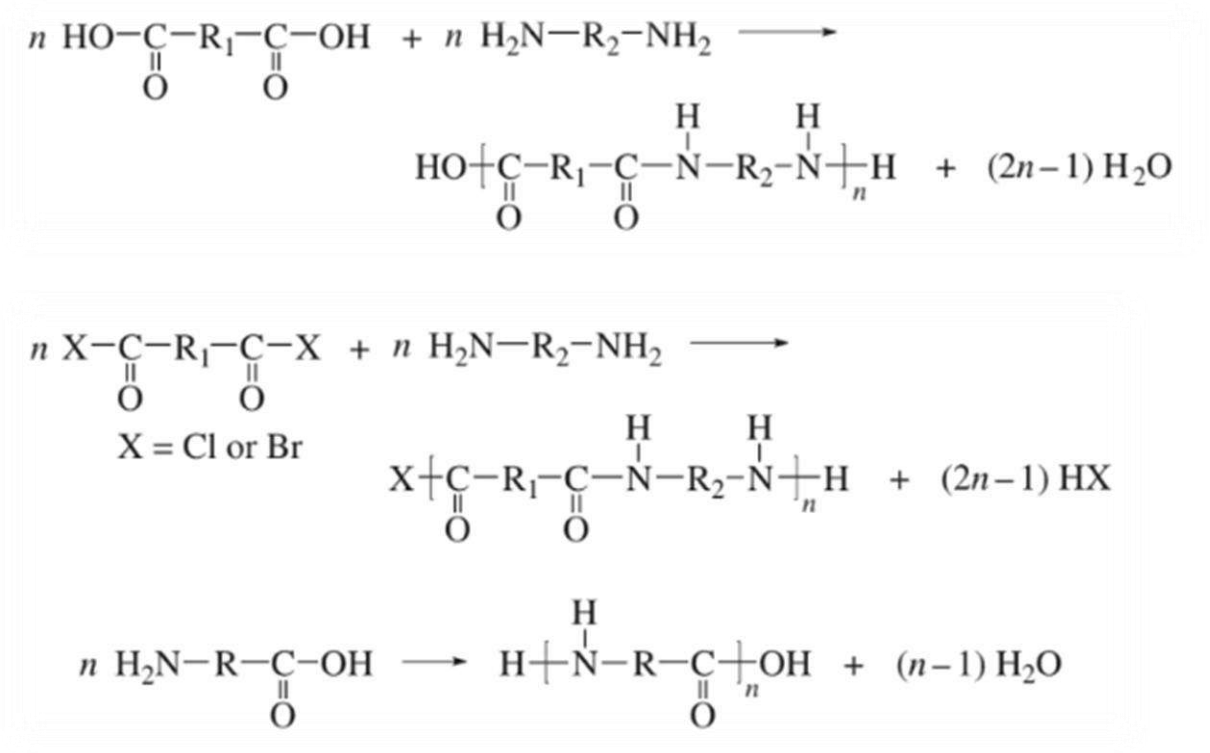


Figure I-10 Polyamide formation

Aliphatic polyamides are called *naylons*, the most important of which are prepared by $RA_2 + RB_2$ polymerization, 6.6 ($R_1 = (CH_2)_4$; $R_2 = (CH_2)_6$ [9].

I.8 Polyaddition

I.8.1 Chain polymerization:

Polymerization chain reactions involve very reactive R * active centers present in very small concentrations. These active centers add in a very short time a large number of monomer molecules (10^3 to 10^5 molecules / s).[10]

I.8.2 Characteristics of chain polymerizations:

The main characteristic of this chain polymerization is that it takes place in 3 phases of which there is a mixture of stages:

The 1st phase is the priming phase: it corresponds to the activation of a molecule of monomer M thanks to an initiator A according to the following equation:

$$A + M \rightarrow M^*$$

M *: the activated monomer or the active center.[11]

This step requires an energy supply by thermal, photochemical or radiochemical routes [12]

The 2nd phase is the propagation phase: it corresponds to the propagation of the active center to other monomers.

$$M^* + M \rightarrow MM^* + M \rightarrow MMM^* \ldots\ldots$$

The 3rd phase is the termination phase: it corresponds to the meeting of a polymer having a monomer activated at the chain end and a species which deactivates this monomer.

Depending on the nature of the active center, any chain polymerization can be classified into one of the following subgroups:

- Radical polymerization: the chain growth agent (the active center) is a free radical generally obtained by homolytic rupture of a covalent bond within the initiator and monomer molecules.

$$A{:}\ B \rightarrow A^{\cdot} + B^{\cdot}$$

- Ionic polymerization (anionic, cationic): in ionic polymerization, the active center is obtained by heterolytic rupture of a covalent bond of an initiator.

- Coordination polymerization (initiated by complexes of transition metals).

I.9 Properties of polymers

I.10 Mechanical properties

Deformation of polymers: the deformation follows the steps:

- Variation of the angles between the carbon atoms in the C-C covalent bonds (Figure 1.3(a-1, a-2)).

- Deployment of the chains which are entangled and folded back on themselves (Figure 1.4(b-1, b-2)).

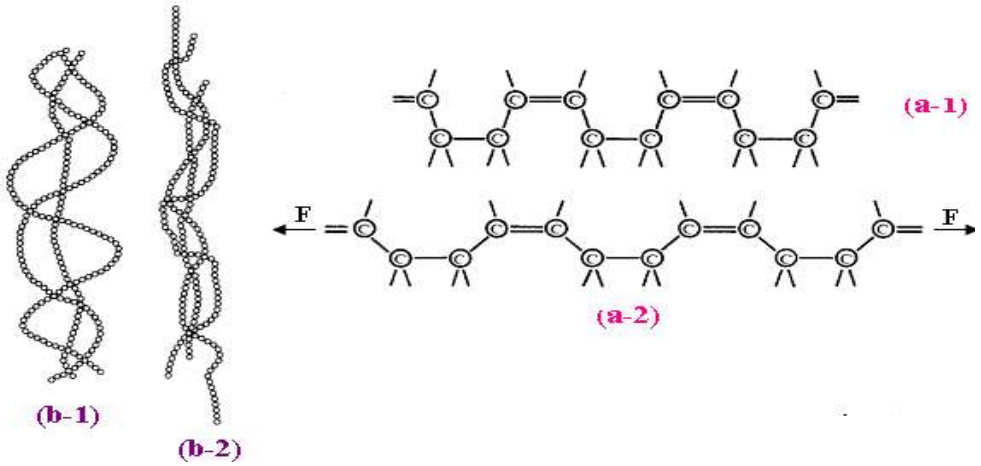


Figure I-11 Stages of polymer deformation

I.10.1 Rigidity of polymers:

- The rigidity of thermoplastics varies greatly with temperature (Figure1.5)

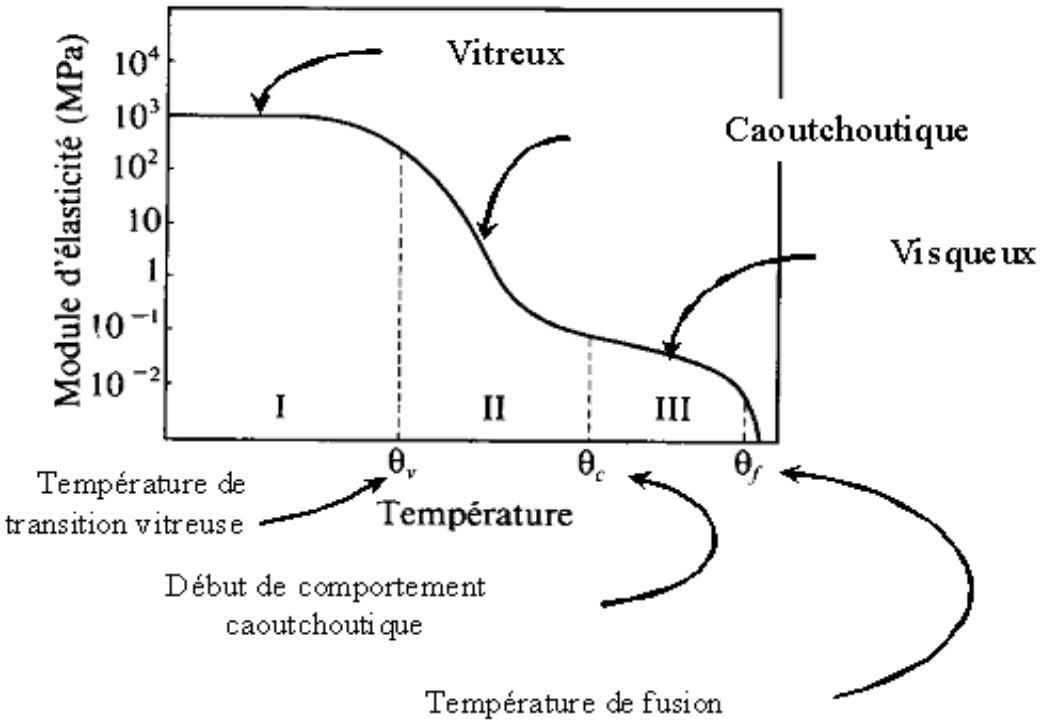


Figure I-12 Temperature effect on phase behavior of glassy polymer

Zone 1: - Glassy state: polymer in a hard and fragile state

Zone 2: - Increased flexibility: rubbery behavior

Zone 3: - Collapse of rigidity: behavior of viscous liquid

● The rigidity of thermosets is important and it is preserved until their degradation

● The rigidity of elastomers is usually very low, it increases with increasing deformation and the number of bridge connections.

1.5.2 / Physical properties: Figure I-12► Thermal properties: low thermal conductivity used as insulators.

► Electrical properties: low conductivity of electrical insulators

► Optical properties: in an amorphous state, polymers transmit light well.not all only transparent ones.

II. HYBRID MATERIALS

II.1 Introduction

Recent technological breakthroughs and the desire for new functions generate an enormous demand for novel materials. Many of the well-established materials, such as metals, ceramics or plastics cannot fulfill all technological desires for the various new applications. Scientists and engineers realized early on that mixture of materials can show superior properties compared with their pure counterparts.

One of the most successful examples is the group of composites which are formed by the incorporation of a basic structural material into a second substance, the *matrix*.

Usually the systems incorporated are in the form of particles, whiskers, fibers, lamellae, or a mesh. Most of the resulting materials show improved mechanical properties and a well-known example is inorganic fiber-reinforced polymers.

Soon it became evident that decreasing the size of the inorganic units to the same level as the organic building blocks could lead to more homogeneous materials that allow a further fine tuning of materials' properties on the molecular and nanoscale level, generating novel materials that either show characteristics in between the two original phases or even new properties. Both classes of materials reveal similarities and differences and an attempt to define the two classes will follow below. However, we should first realize that the origin of hybrid materials did not take place in a chemical laboratory but in nature.

II.2 Natural origins

Many natural materials consist of inorganic and organic building blocks distributed on the (macro) molecular or nanoscale. In most cases the inorganic part provides mechanical strength and an overall structure to the natural objects while the organic part delivers bonding between the inorganic building blocks and/or the soft tissue.

The concepts of bonding and structure in such materials are intensively studied by many scientists to understand the fundamental processes of their formation and to transfer the ideas to artificial materials in a so-called biomimetic approach. In particular the study of biomineralization and its shape control is an important target of many scientific studies. This primarily interface-controlled process still reveals many questions, in particular how such a remarkable level of morphological diversity with a multiplicity of functions can be produced by so few building blocks.

In addition to questions concerning the composition of the materials, their unique structures motivate inquiry to get a deeper insight in their formation, often not only because of their beauty but also because of the various functions that the structures perform. A complex hierarchical order of construction from the nanometer to the millimeter level is regularly found in nature, where every size level of the specific material has its function which benefits the whole performance of the material. Furthermore these different levels of complexity are reached by soft chemical self-assembly mechanisms over a large dimension, which is one of the major challenges of modern materials chemistry.

II.3 Development of Hybrid Materials

Although we do not know the original birth of hybrid materials exactly, it is clear that the mixing of organic and inorganic components was carried out in ancient world. At that time the production of bright and colorful paints was the driving force to consistently try novel mixtures of dyes or inorganic pigments and other inorganic and organic components to form paints that were used thousands of years ago. Therefore, hybrid materials or even nanotechnology is not an invention of the last decade but was developed a long time ago. However, it was only at the end of the 20th and the beginning of the 21st century that it was realized by scientists, in particular because of the availability of novel physic chemical characterization methods, the field of nanoscience opened many perspectives for approaches to new materials. The combination of different analytical techniques gives rise to novel insights into hybrid materials and makes it clear that bottomup strategies from the molecular level towards materials' design will lead to novel properties in this class of materials.[13]

Apart from the use of inorganic materials as fillers for organic polymers, such as rubber, it was a long time before much scientific activity was devoted to mixtures of inorganic and organic materials. One process changed this situation: the sol–gel process. This process, which will be discussed in more detail later on, was developed in the 1930s using silicon alkoxides as precursors from which silica was produced. In fact, this process is similar to an organic polymerization starting from molecular precursors resulting in a bulk material. Contrary to many other procedures used in the production of inorganic materials, this is one of the first processes where ambient conditions were applied to produce ceramics. The control over the preparation of multicomponent systems by a mild reaction method also led to industrial interest in that process. In particular the silicon based sol–gel process was one of the major driving forces what has become the broad field of inorganic– organic hybrid materials. The reason for the special role of silicon was its good process ability and the stability of the Si—C bond during the formation of a silica network which allowed the production of organic-modified inorganic networks in one step.

Inorganic–organic hybrids can be applied in many branches of materials chemistry because they are simple to process and are amenable to design on the molecular scale. Currently there are four major topics in the synthesis of inorganic– organic materials: (a) their molecular engineering, (b) their nanometer and micrometer-sized organization, (c) the transition from functional to multifunctional hybrids, and (d) their combination with bioactive components.

Some similarities to sol–gel chemistry are shown by the stable metal sols and colloids, such as gold colloids, developed hundreds of years ago. In fact, sols prepared by the sol–gel process, i.e. the state of matter before gelation, and the gold colloids have in common that their building blocks are nanosized particles surrounded by a (solvent) matrix. Such metal colloids have been used for optical applications in nanocomposites for centuries. Glass, for example, was already colored with such colloids centuries ago. In particular many reports of the scientific examination of gold colloids, often prepared by reduction of gold salts, are known from the end of the 18th century. Probably the first nanocomposites were produced in the middle of the 19th century when gold salts were reduced in the presence of gum arabic. Currently many of the colloidal systems already known are being reinvestigated by modern

instrumental techniques to get new insights into the origin of the specific chemistry and physics behind these materials.

II.4 Definition Hybrid Materials and Nanocomposites

The term hybrid material is used for many different systems spanning a wide area of different materials, such as crystalline highly ordered coordination polymers, amorphous sol–gel compounds, materials with and without interactions between the inorganic and organic units. Before the discussion of synthesis and properties of such materials we try to delimit this broadly-used term by taking into account various concepts of composition and structure (Table II-1). The most wide-ranging apart from the use of inorganic materials as fillers for organic polymers, such as rubber, it was a long time before much scientific activity was devoted to mixtures of inorganic and organic materials. One process changed this situation: the sol–gel process. This process, which will be discussed in more detail later on, was developed in the 1930s using silicon alkoxides as precursors from which silica was produced. In fact this process is similar to an organic polymerization starting from molecular precursors resulting in a bulk material[14]. Contrary to many other procedures used in the production of inorganic materials this is one of the first processes where ambient conditions were applied to produce ceramics.[15].

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T**Table II-1 Different possibilities of composition and structure of hybrid materials.**

Matrix	crystalline amorphous organic inorganic
Building blocks	molecules macromolecules particles fibers
Interactions between components	strong weak

Definition is the following: a hybrid material is a material that includes two moieties blended on the molecular scale. Commonly one of these compounds is inorganic and the other one organic in nature. A more detailed definition distinguishes between the possible interactions connecting the inorganic and organic species. *Class I* hybrid materials are those that show weak interactions between the two phases, such as Van der Waals, hydrogen bonding or weak electrostatic interactions.[18] *Class II* hybrid materials are those that show strong chemical interations between the components. Because of the gradual change in the strength of chemical interactions it becomes clear that there is a steady transition between weak and strong interactions (Fig. 1.1). For example there are

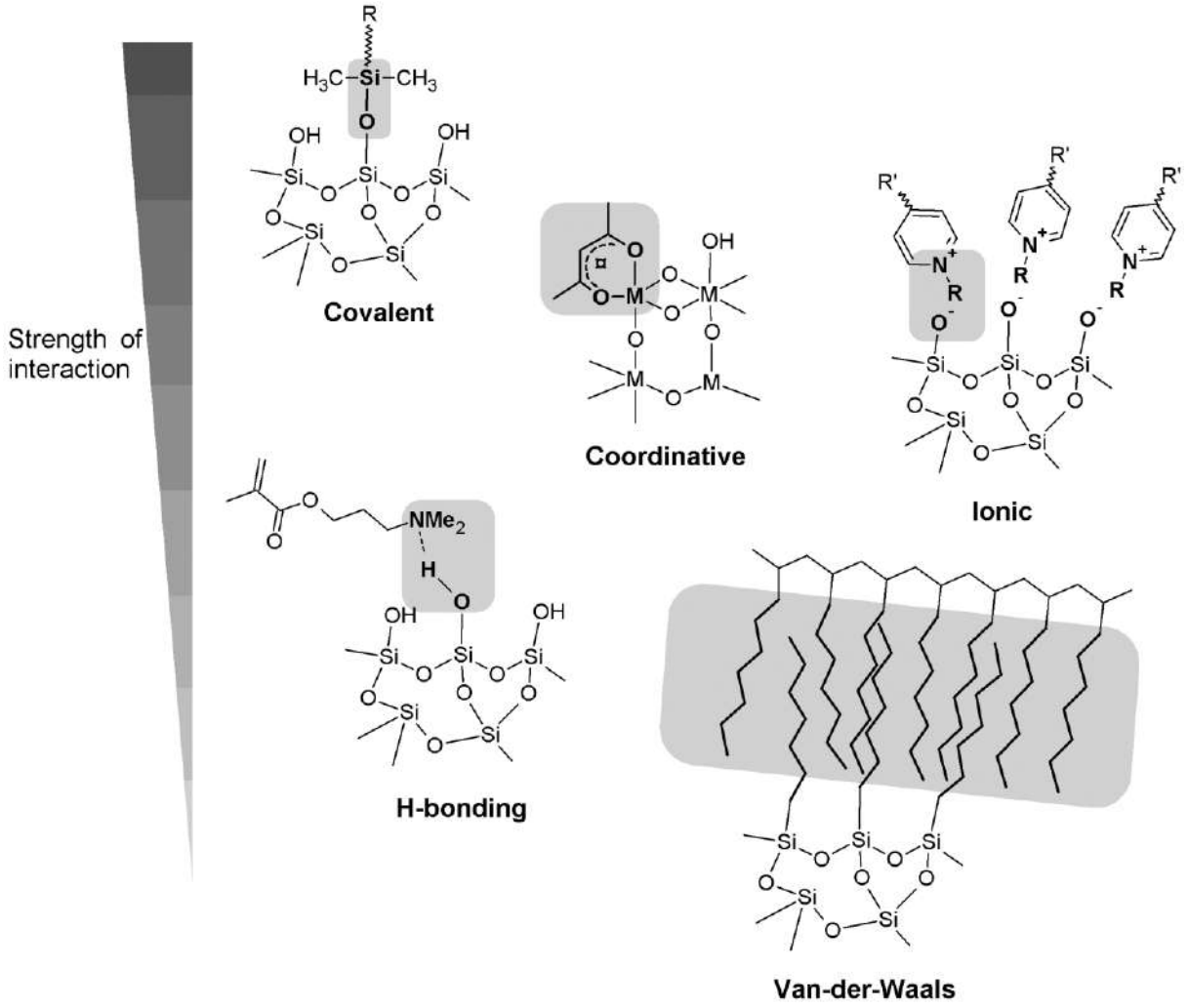


Figure II-1 Selected interactions typically applied in hybrid materials and their relative strength.

Table II-2 Different chemical interactions and their respective strength reference.

Type of interaction	***Strength [kJmol−1]***	***Range***	***Character***
van der Waals	ca. 50	Short	nonselective, nondirectional

H-bonding	5–65	Short	selective, directional
Ionic	50–250[a0	Short	nonselective
Coordination bonding	50–200	Long	directional
Covalent	350	Short	predominantly Irreversible

a Depending on solvent and ion solution; data are for organic media.

The situation is different if two or three of such anchor groups modify an organic segment; this leads to materials in which the inorganic group is afterwards an integral part of the hybrid network (**Error! Reference source not found.**). Blends are formed if no strong c hemical interactions exist between the inorganic and organic building blocks. One example for such a material is the combination of inorganic clusters or particles with organic polymers lacking a strong (e.g. covalent) interaction between the components (Figure II-3). In this case a material is formed that consists for example of an organic polymer with entrapped discrete inorganic moieties in which, depending on the functionalities of the components, for example weak crosslinking occurs by the entrapped inorganic units through physical interactions or the inorganic components are entrapped in a crosslinked polymer matrix. If an inorganic and an organic network interpenetrate each other without strong chemical interactions, so called interpenetrating networks (IPNs) are formed (Figure II-3), which is for example the case if a sol–gel material is formed in presence of an organic polymer or vice versa.[19]

Both materials described belong to class I hybrids. Class II hybrids are formed when the discrete inorganic building blocks, e.g. clusters, are covalently bonded to the organic polymers (Figure II-3) or inorganic and organic polymers are covalently connected with each other (Figure II-3).

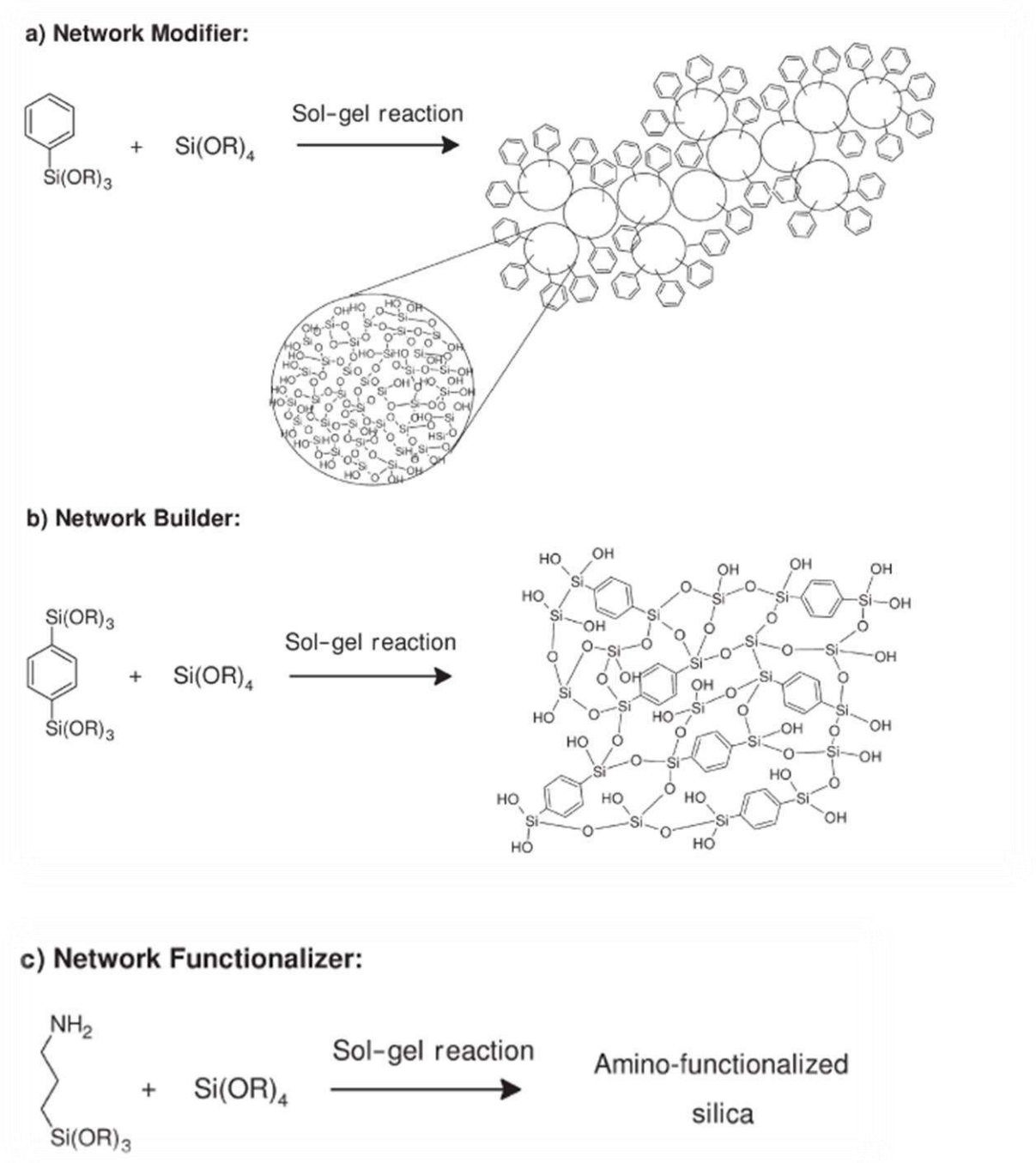


Figure II-2 Role of organically functionalized trialkoxysilanes in the silicon-based sol-gel process

Nanocomposites

The term nanocomposite is used if one of the structural units, either the organic or the inorganic, is in a defined size range of 1–100 nm. Therefore there is a gradual transition between hybrid materials and nanocomposites,

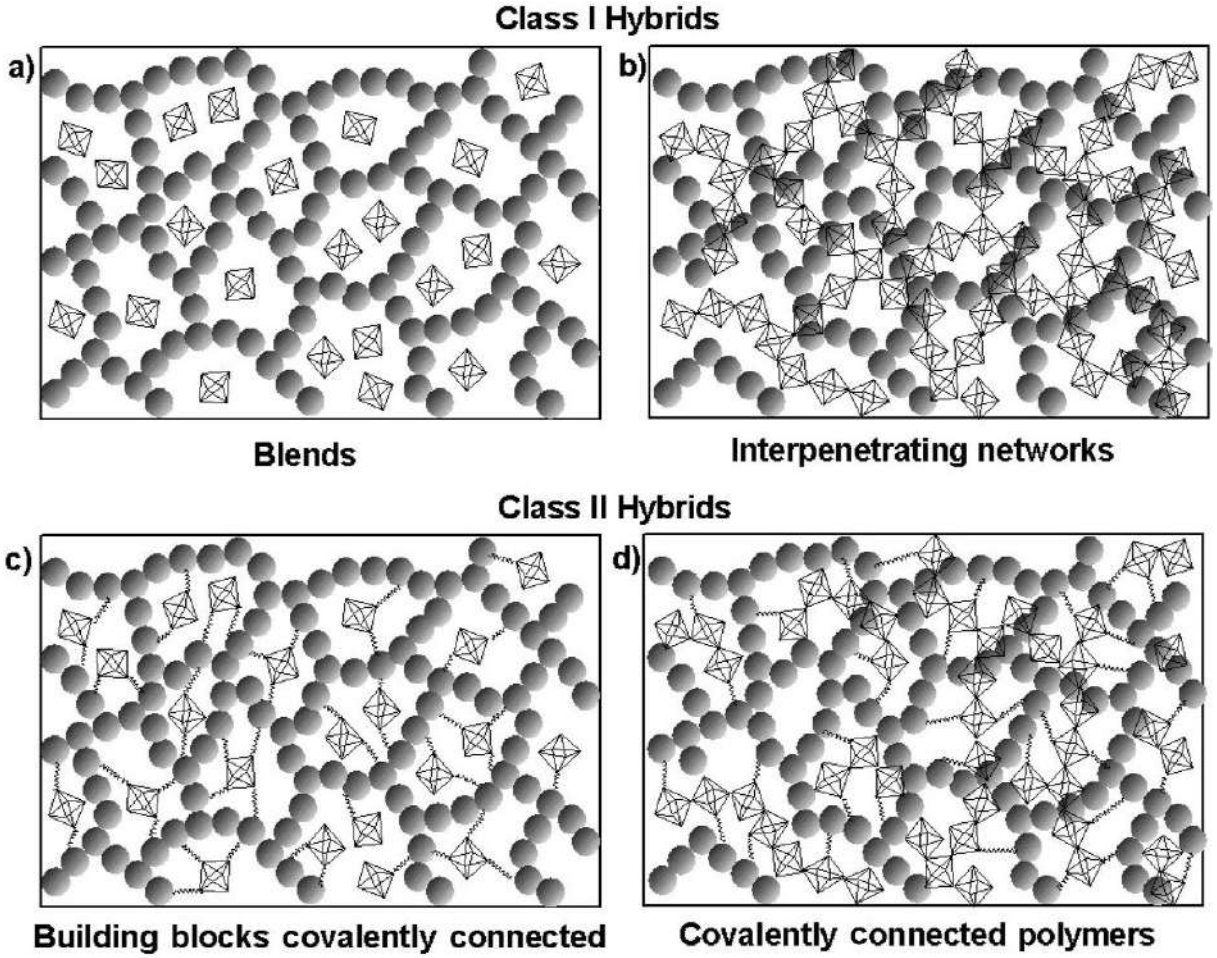


Figure II-3 The different types of hybrid materials.

because large molecular building blocks for hybrid materials, such as large inorganic clusters, can already be of the nanometer length scale. Commonly the term nanocomposites is used if discrete structural units in the respective size regime are used and the term hybrid materials is more often used if the inorganic units are formed *in situ* by molecular precursors, for example applying sol–gel reactions.[20]

Examples of discrete inorganic units for nanocomposites are nanoparticles, nanorods, carbon nanotubes and galleries of clay minerals (Figure II-3)Usually a nanocomposite is formed from these building blocks by their incorporation in organic polymers.

II.5 Advantages of Combining Inorganic and Organic Species in One Material

The most obvious advantage of inorganic–organic hybrids is that they can favorably combine the often dissimilar properties of organic and inorganic components in one material (Table II-3). Because of the many possible combinations of components this field is very creative, since it provides the opportunity to invent an almost unlimited set of new materials with a large spectrum of known and as yet unknown properties. Another driving force in the area of hybrid materials is the possibility to create multifunctional materials

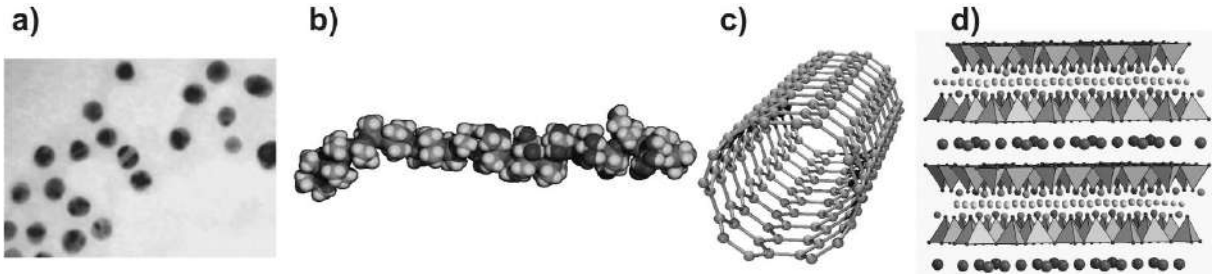


Figure II-4 Inorganic building blocks used for embedment in anorganic matrix in the preparation of inorganic-organicnanocomposites: a) nanoparticles, b) macromolecules,c) nanotubes, d) layered materials.

Table II-3 Comparison of general properties of typical inorganic and organic materials.[21]

Properties	***Organics (polymers)***	***Inorganics (SiO2, transition metal oxides (TMO))***
Nature of bonds	covalent [C—C], van der Waals, H-bonding	ionic or iono-covalent [M—O]
*T*g	low (−120 °C to 200 °C)	high (>>200°C)
Thermal stability	low (<350 °C–450 °C)	high (>>100°C)
Density	0.9–1.2	2.0–4.0
Refractive index	1.2–1.6	1.15–2.7
Mechanical properties	elasticity plasticity rubbery (depending on *T*g)	hardness strength fragility
Hydrophobicity	Hydrophilic	hydrophilic
Permeability	Hydrophobic ±permeable to gases	low permeability to gases
Electronic properties	insulating to conductive insulating to semiconductors redox properties	insulating to semiconductors redox properties (SiO2, TMO) magnetic properties
Processability	high (molding, casting, film formation, control of viscosity)	low for powders fhigh for sol–gel coatings

Probably the most intriguing property of hybrid materials that makes this material class interesting for many applications is their processing. Contrary to pure solid state inorganic materials that often require a high temperature treatment for their processing, hybrid materials show a more polymer-like handling, either because of their large organic content or because of the formation of crosslinked inorganic networks from small molecular precursors just like in polymerization reactions. Hence, these materials can be shaped in any form in bulk and in films. Although from an economical point of view bulk hybrid materials can currently only compete in very special areas with classical inorganic or organic materials,

Mechanical properties, such as toughness or scratch resistance, are tailored if hard inorganic nanoparticles are included into the polymer matrix..

One important subject in materials chemistry is the formation of smart materials, such as materials that react to environmental changes or switchable systems, One of the advantages of hybrid materials in this context is that functional organic molecules as well as biomolecules often show better stability and performance if introduced in an inorganic matrix.

II.6 Interface-determined Materials

The transition from the macroscopic world to microscopic, nanoscopic and molecular objects leads, beside the change of physical properties of the material itself, i.e. the so called quantum size effects, to the change of the surface area of the objects. While in macroscopic materials the majority of the atoms is hidden in the bulk of the material it becomes vice versa in very small objects. This is demonstrated by a simple mind game (Figure II-5). If one thinks of a cube of atoms in tight packing of 16 × 16 × 16 atoms. . In small nanoparticles (<10nm) nearly every atom is a surface atom that can interact with the environment. One predominant feature of hybrid materials or nanocomposites is their inner interface.

If the two phases have opposite properties, such as different polarity, the system would thermodynamically phase separate. The same can happen on the molecular or nanometer level, leading to microphase separation.

Usually, such a system would thermodynamically equilibrate over time. However in many cases in hybrid materials the system is kinetically stabilized by networkforming reactions such as the sol–gel process leading to a spatial fixation of the structure. The materials formed can be macroscopically homogeneous and optically clear, because the phase segregation is of small length scale and therefore limited interaction with visible light occurs. However, the composition on the molecular or nanometer length scale can be heterogeneous. If the phase segregation reaches the several hundred nanometer length scale or the refractive index of the formed domains is very different, materials often turn opaque. Effects like this are avoided if the reaction parameters are controlled in such a way that the speed of network formation is kept faster than the phase separation reactions.

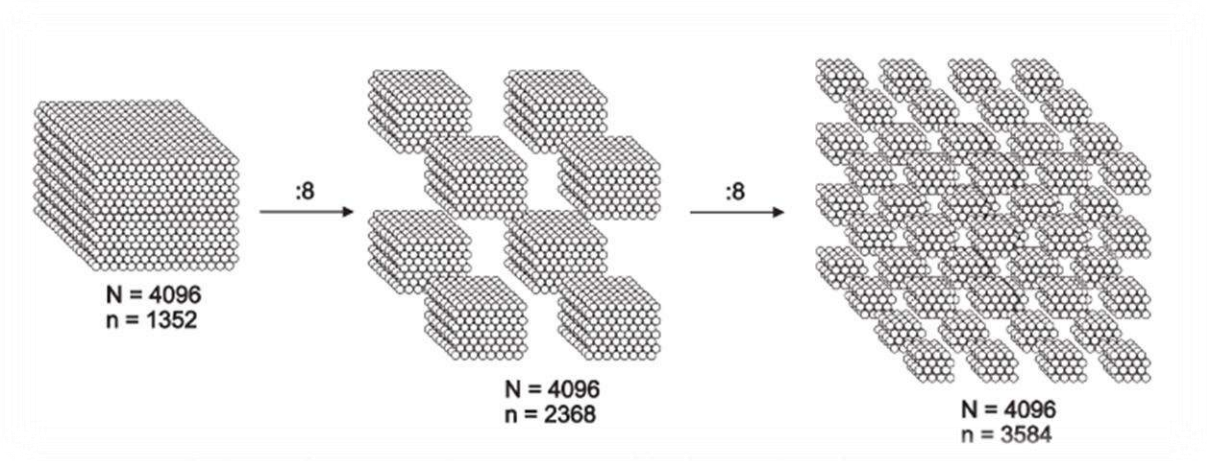


Figure II-5 Surface statistical consequences of dividing a cube

The high surface area of nanobuilding blocks can lead to additional effects; for example if surface atoms strongly interact with molecules of the matrix by chemical bonding, Nanosized objects, such as inorganic nanoparticles, in addition show a very high surface energy. Usually if the surface energy is not reduced by surface active agents (e.g. surfactants), such particles tend to agglomerate in an organic medium. Thus, the physical properties of the nanoparticles (e.g. quantum size effects) diminish, and/or the resulting materials are no longer homogeneous. Both facts have effects on the final material properties.

II.7 The Role of the Interaction Mechanisms

the interaction mechanism between the organic and inorganic species was used to categorize the different types of hybrid materials, furthermore of course the interaction also has an impact on the material properties. Weak chemical interactions between the inorganic and organic entities leave some potential for dynamic phenomena in the final materials, meaning that over longer periods of time changes in the material, such as aggregation, phase separation or leaching of one of the components, can occur. These phenomena can be avoided if strong interactions are employed such as covalent bonds, as in nanoparticle crosslinked polymers. Depending on the desired materials' properties the interactions can be gradually tuned. Weak interactions are, for example, preferred where a mobility of one component in the other is required for the target properties.

In addition the interaction of the two components can have an influence on other properties, such as electronic properties if coordination complexes are formed or electron transfer processes are enabled by the interaction.

II.8 Synthetic Strategies towards Hybrid Materials

In principle two different approaches can be used for the formation of hybrid materials: Either well-defined preformed building blocks are applied that react with each other to form the final hybrid material in which the precursors still at least partially keep their original integrity or one or both structural units are formed from the precursors that are transformed into a novel (network) structure. .

Building block approach As mentioned above building blocks at least partially keep their molecular integrity throughout the material formation, which means that structural units that are present in these sources for materials formation can also be found in the final

material. At the same time typical properties of these building blocks usually survive the matrix formation, which is not the case if material precursors are transferred into novel materials. Figure II-6).

Cluster compounds often consist of at least one functional group that allows an interaction with an organic matrix, for example by copolymerization. Depending on the number of groups that can interact, these building blocks are able to modify an organic matrix (one functional group) or form partially or fully crosslinked materials (more than one group). For instance, two reactive groups can lead to the formation of chain structures. If the building blocks contain at least three reactive groups they can be used without additional molecules for the formation of a crosslinked material.[22]

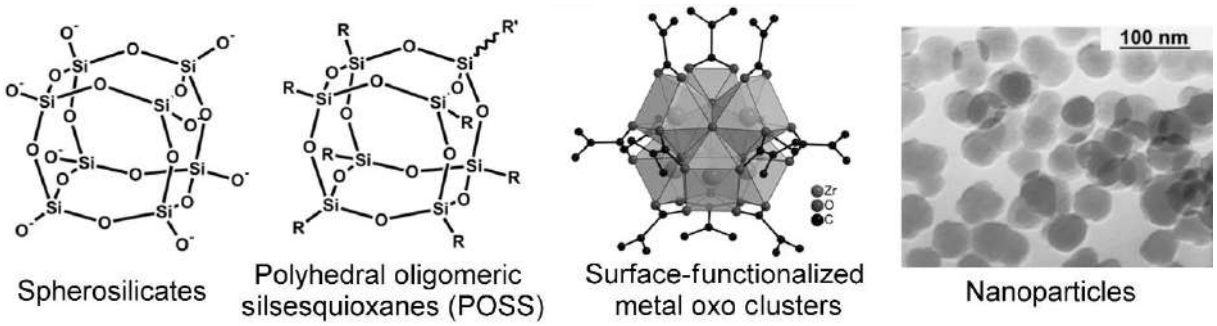


Figure II-6 Typical well-defined molecular building blocks used in the formation of hybrid materials

Beside the molecular building blocks mentioned, nanosized building blocks, such as particles or nanorods, can also be used to form nanocomposites. The building block approach has one large advantage compared with the *in situ* formation of the inorganic or organic entities. Furthermore, the building blocks can be designed in such a way to give the best performance in the materials' formation.

In situ formation of the components Contrary to the building block approach is based on the chemical transformation of the precursors used throughout materials' preparation. Typically, this is the case if organic polymers are formed but also if the sol–gel process is applied to produce the inorganic component. . Generally simple, commercially available molecules are applied and the internal structure of the final material is determined by the composition of these precursors but also by the reaction conditions. Therefore, control over the latter is a crucial step in this process. Changing one parameter can often lead to two very different materials. I. Hence, the final performance of the derived materials is strongly dependent on their processing and its optimization.

II.8.1 In situ Formation of Inorganic Materials

Many of the classical inorganic solid state materials are formed using solid precursors and high temperature processes, which are often not compatible with the presence of organic groups because they are decomposed at elevated temperatures.

Hence, these high temperature processes are not suitable for the *in situ* formation of hybrid materials. Reactions that are employed should have more the character of classical covalent bond formation in solutions. One of the most prominent processes which fulfill these demands is the sol–gel process. .

II.8.2 Sol–Gel Process

This process is chemically related to an organic polycondensation reaction in which small molecules form polymeric structures by the loss of substituents. Usually the reaction results in a three-dimensional (3-D) crosslinked network. The fact that small molecules are used as precursors for the formation of the crosslinked materials implies several advantages, for example a high control of the purity and composition of the final materials and the use of a solvent based chemistry which offers many advantages for the processing of the materials formed.

The silicon-based sol–gel process is probably the one that has been most investigated; therefore, the fundamental reaction principles are discussed using this process as a model system. One important fact also makes the silicon-based sol–gel processes a predominant process in the formation of hybrid materials, which is the simple incorporation of organic groups using organically modified silanes.[23]

Si—C bonds have enhanced stability against hydrolysis in the aqueous media usually used, which is not the case for many metal–carbon bonds, so it is possible to easily incorporate a large variety of organic groups in the network formed. Principally

R4–nSiXn compounds (n = 1–4, X = OR', halogen) are used as molecular precursors, in which the Si—X bond is labile towards hydrolysis reactions forming unstable silanols (Si—OH) that condensate leading to Si—O—Si bonds. In the first steps of this reaction oligo- and polymers as well as cyclics are formed subsequently resulting in colloids that define the sol. Solid particles in the sol afterwards undergo crosslinking reactions and form the gel (**Error! Reference source not found.**).[24]

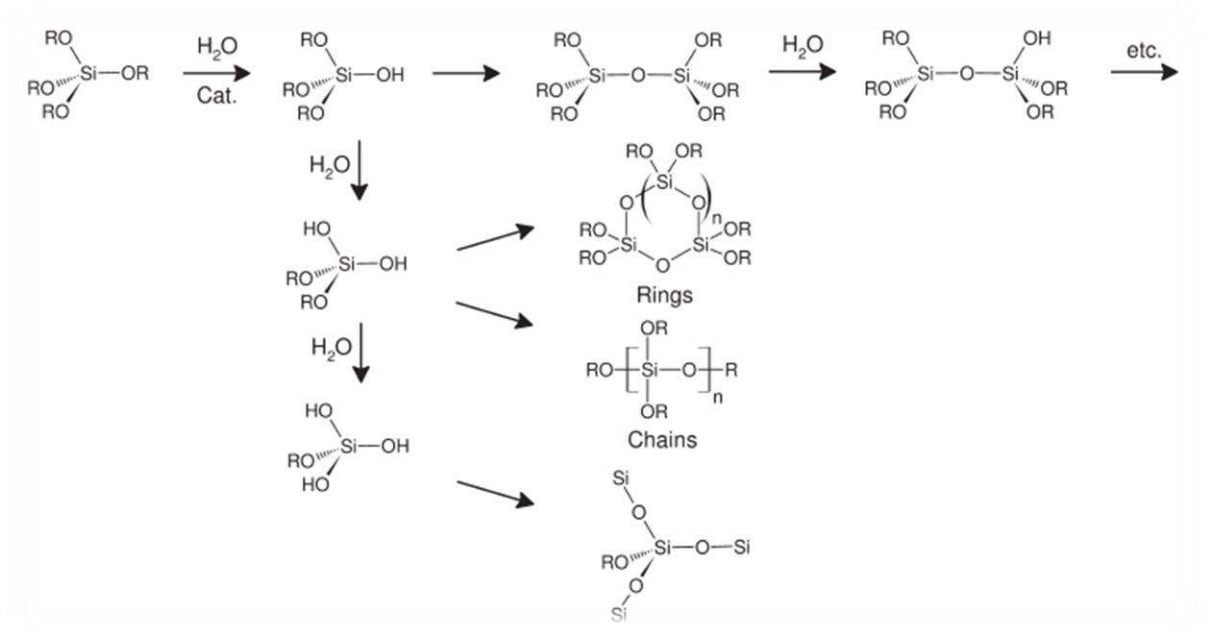


Figure II-7 fundamental reaction steps in the sol–gel process based on tetrialkoxysilanes

The process is catalyzed by acids or bases resulting in different reaction mechanisms by the velocity of the condensation reaction (Figure II-8). The pH used therefore has an effect on the kinetics which is usually expressed by the gel point of the sol–gel reaction. The reaction is slowest at the isoelectric point of silica (between 2.5 and 4.5 depending on different parameters) and the speed increases rapidly on changing the pH. Not only do the reaction conditions have a strong influence on the kinetics of the reaction but also the structure of the precursors.

Generally, larger substituents decrease the reaction time due to steric hindrance.

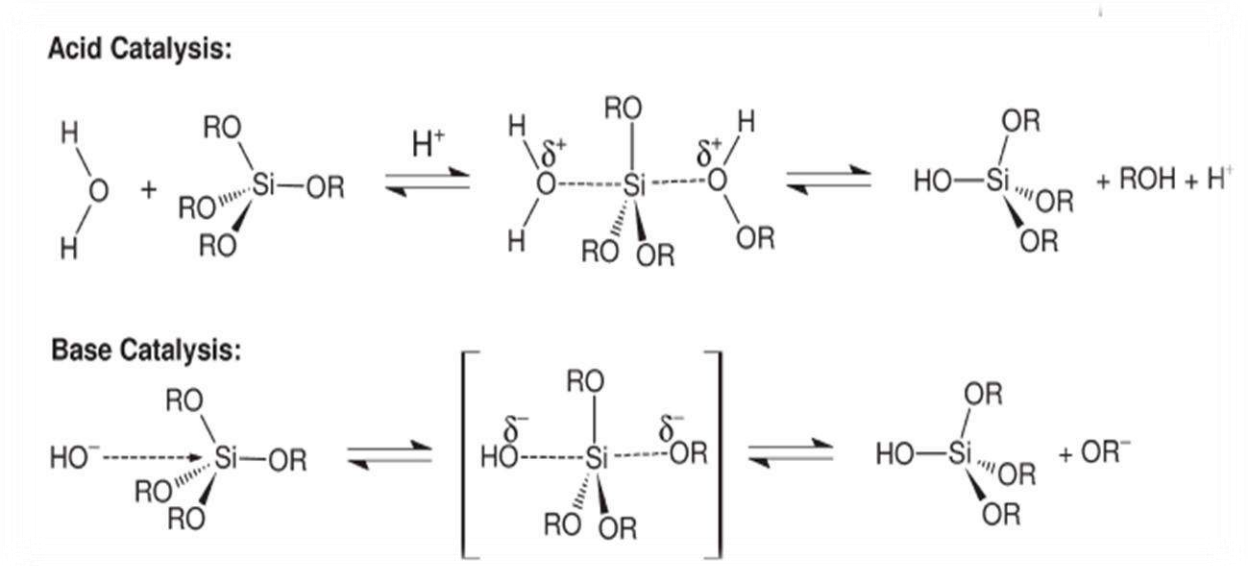


Figure II-8 Differences in mechanism depending on the type

In addition, the substituents play a mature role in the solubility of the precursor in the solvent. Water is required for the reaction and if the organic substituents are quite large usually the precursor becomes immiscible in the solvent. By changing the solvent one has to take into account that it can interfere in the hydrolysis reaction, for example alcohols can undergo *trans*-esterification reactions leading to quite complicated equilibria in the mixture. Hence, for a well-defined material the reaction conditions have to be fine-tuned.[25]

The pH not only plays a major role in the mechanism but also for the microstructure of the final material. Applying acid-catalyzed reactions an open network structure is formed in the first steps of the reaction leading to condensation of small clusters afterwards. Contrarily, the base-catalyzed reaction leads to highly crosslinked sol particles already in the first steps. This can lead to variations in the homogeneity of the final hybrid materials as will be shown later. Commonly used catalysts are $HCl, NaOH$ or $NH4OH$, but fluorides can be also used as catalysts leading to fast reaction times.

The transition from a sol to a gel is defined as the gelation point, which is the point when links between the sol particles are formed to such an extent that a solid material is obtained containing internal pores that incorporate the released alcohol. However, at this point

the reaction has not finished, but condensation reactions can go on for a long time until a final stage is reached. This process is called ageing. During this reaction the material shrinks and stiffens. This process is carried on in the drying process, where the material acquires a more compact structure and the associated crosslinking leads to an increased stiffness. During the drying process the large capillary forces of the evaporating liquids in the porous structure take place which can lead to cracking of the materials. Reaction parameters such as drying rate, gelation time, pH, etc. can have a major influence on the cracking of the gels and have therefore to be optimized. Under some circumstances the destruction of the gel network can lead to the formation of powders instead of monoliths during materials formation.

Stress during the drying process can be avoided if the liquid in the pores is exchanged under supercritical conditions where the distinction between liquid and vapor no longer exists. This process leads to so-called highly porous aerogels compared with the conventionally dried xerogels.

As already mentioned above many parameters influence the speed of the sol–gel reaction; if a homogeneous material is required all parameters must be optimized.

This is particularly true if hybrid materials are the target, because undesired phase separations of organic and inorganic species in the materials or between the network and unreacted precursors weaken the materials' properties. This can often even be observed by the naked eye if the material turns opaque.

The water to precursor ratio is also a major parameter in the sol–gel process. If tetraalkoxysilanes are used as precursors, two water molecules per starting compound are necessary to form completely condensed SiO2. Applying a lower H2O/Si ratio, would lead to an alkoxide containing final material.

II.8.2.1 Nonhydrolytic Sol–Gel Process

In this process the reaction between metal halides and alkoxides is used for the formation of the products (Figure II-9). The alkoxides can be formed during the process by various reactions. Usually this process is carried out in sealed tubes at elevated temperature but it can also be employed in unsealed systems under an inert gas atmosphere.

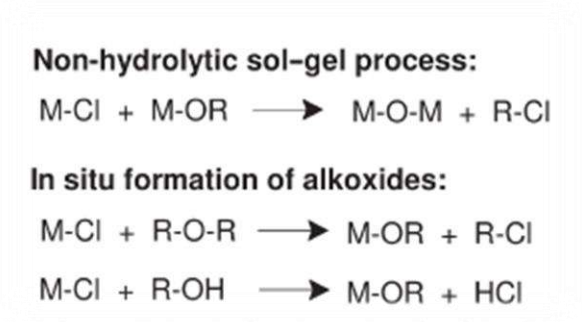


Figure II-9 Mechanisms involved in the nonhydrolytic sol–gel process

II.8.2.2 Sol–Gel Reactions of Non-Silicates

Metal and transition-metal alkoxides are generally more reactive towards hydrolysis and condensation reactions compared with silicon. The metals in the alkoxides are usually in their highest oxidation state surrounded by electronegative –OR ligands which render them

susceptible to nucleophilic attack. Transition metal alkoxides show a lower electronegativity compared with silicon which causes them to be more electrophilic and therefore less stable towards hydrolysis in the sol–gel reactions. Furthermore, transition metals often show several stable coordination environments. While the negatively charged alkoxides balance the charge of the metal cation, they generally cannot completely saturate the coordination sphere of

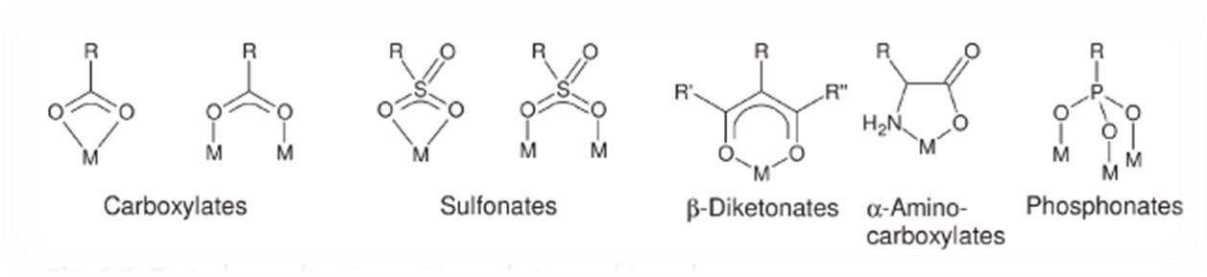


Figure II-10 Typical coordination patterns between bi- and multidentate ligands and metals that can be applied for the incorporation of organic functionalities in metal oxides

the metals, which leads to the formation of oligomers via alkoxide or alcohol bridges and/or the saturation of the coordination environment by additional coordination of alcohol molecules, which also has an impact on the reactivity of the metal alkoxides. More sterically demanding alkoxides, such as isopropoxides, lead to a lower degree of aggregation and smaller alkoxides, such as ethoxides or *n*-propoxides, to a larger degree of aggregation. In addition, the length of the alkyl group in the metal alkoxides also influences their solubility in organic solvents, for example ethoxides often show a much lower solubility as their longer alkyl chain containing homologs.

As already mentioned M—C bonds in metal alkoxides are in most cases not stable enough to survive the sol–gel conditions. Therefore, contrary to the silica route, other mechanisms have to be employed if it is desired that hybrid inorganic–organic metal oxide materials be formed in a one-step approach. One solution to the latter problem is the use of organically functionalized bi- and multidentate ligands that show a higher bonding stability during the sol–gel reaction and, in addition, reduce the speed of the reaction by blocking coordination sites (Fig. 1.5).[26]

II.8.2.3 Hybrid Materials by the Sol–Gel Process

Organic molecules other than the solvent can be added to the sol and become physically entrapped in the cavities of the formed network upon gelation. For this purpose, the molecules have to endure the reaction conditions of the sol–gel process, namely the aqueous conditions and the pH of the environment. Hence, functional organic groups that can be hydrolyzed are not tolerated, but a partial tolerance for the pH can be obtained if the sol–gel reaction is carried out in a buffer solution.

This is particularly necessary if biological molecules, such as enzymes, are to be entrapped in the gel. Physical entrapment has the disadvantage that sometimes the materials obtained are not stable towards phase separation or leaching because of differences in

polarity. Chemical modification of organic compounds with trialkoxysilane groups can partially avoid such problems due to co-condensation during the formation of the sol–gel network and thus development of covalent linkages to the network. Trialkoxysilane groups are typically introduced by a platinum catalyzed reaction between an unsaturated bond and a trialkoxysilane (Scheme 1.6).[27]

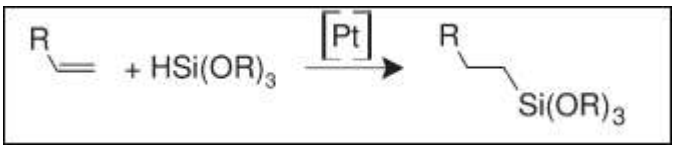


Figure II-11 Platinum catalyzed hydrosilation for the introduction of trialkoxysilane groups.

Besides the entrapment of organic systems, precursors with hydrolytically stable Si—C bonds can also be used for co-condensation reactions with tetraalkoxysilanes.

In addition, organically functionalized trialkoxysilanes can also be used for the formation of 3-D networks alone forming so called silsesquioxanes (general formula R-SiO1.5) materials. Generally a 3-D network can only be obtained if three or more hydrolyzable bonds are present in a molecule. Two such bonds generally result in linear products and one bond leads only to dimers or allows a modification of a preformed network by the attachment to reactive groups on the surface of the inorganic network (Fig. 1.6). Depending on the reaction conditions in the sol–gel process smaller species are also formed in the organotrialkoxysilane based sol–gel process, for example cage structures or ladder-like polymers (Fig. 1.6). Because of the stable Si—C bond the organic unit can be included within the silica matrix without transformation are shown in (Figure II-12)

Usually the organic functionalizations have a large influence on the properties of the final hybrid material. First of all, the degree of condensation of a hybrid material prepared by trialkoxysilanes is generally smaller than in the case of tetraalkoxysilanes and thus the network density is also reduced.

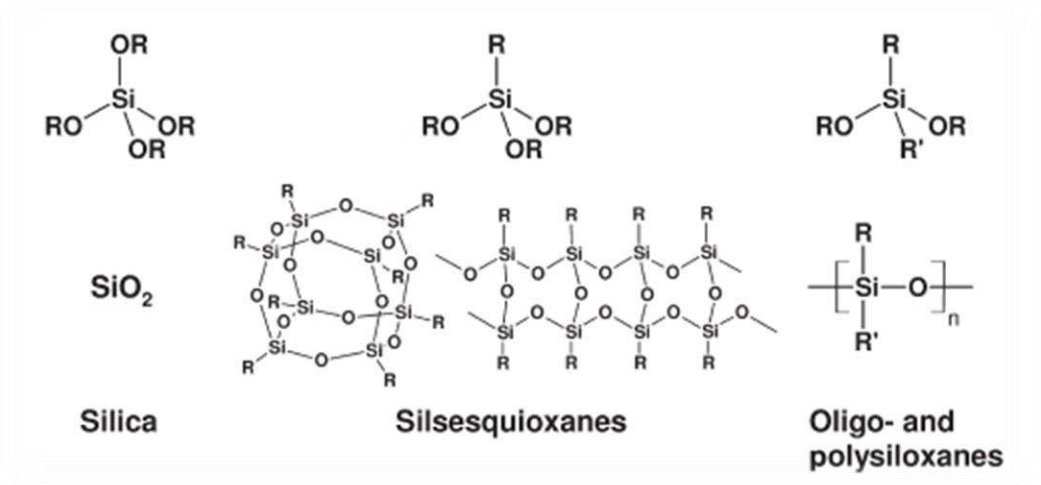


Figure II-12 Formation of different structures during hydrolysis independence of the number of organic substituents compared tolabile substituents at the silicon atom.

In addition, the functional group incorporated changes the properties of the final material, for example fluoro-substituted compounds can create hydrophobic and lipophobic materials, additional reactive functional groups can be introduced to allow further reactions such as amino, epoxy or vinyl groups (Figure II-13)

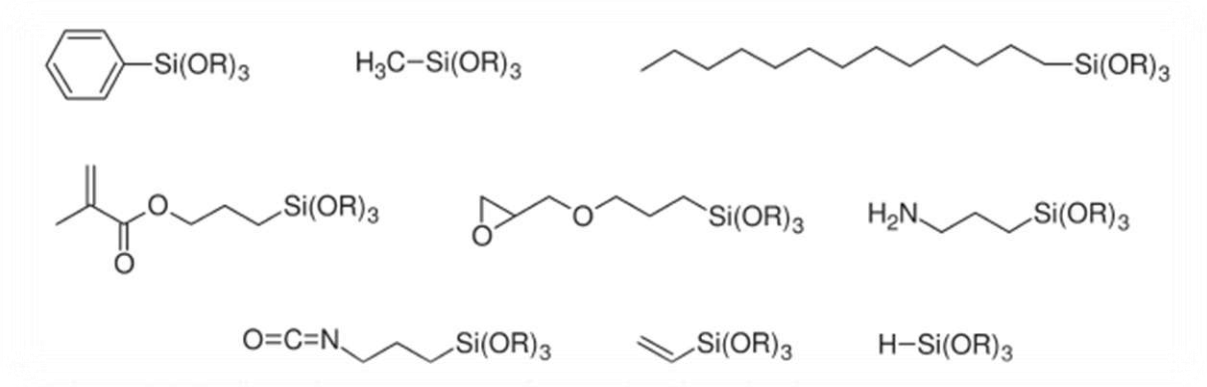


Figure II-13 Trialkoxysilane precursors often used in the sol–gel process.

II.8.2.4 Hybrid Materials Derived by Combining the Sol–Gel Approach and Organic Polymers

Compared with other inorganic network forming reactions, the sol–gel processes show mild reaction conditions and a broad solvent compatibility. These two characteristics offer the possibility to carry out the inorganic network forming process in presence of a preformed organic polymer or to carry out the organic polymerization before, during or after the sol–gel process. The properties of the final hybrid materials are not only determined by the properties of the inorganic and organic component, but also by the phase morphology and the interfacial region between the two components. The often dissimilar reaction mechanisms of the sol–gel process and typical organic polymerizations, such as free radical polymerizations, allow the temporal separation of the two polymerization reactions which offers many advantages in the material formation.

One major parameter in the synthesis of these materials is the identification of a solvent in which the organic macromolecules are soluble and which is compatible with either the monomers or preformed inorganic oligomers derived by the sol–gel approach. Many commonly applied organic polymers, such as polystyrene or polymethacrylates, are immiscible with alcohols that are released during the sol–gel process and which are also used as solvents, therefore phase separation is enforced in these cases. This can be avoided if the solvent is switched from the typically used alcohols to, for example, THF in which many organic polymers are soluble and which is compatible with many sol–gel reactions. Phase separation can also be avoided if the polymers contain functional groups that are more compatible with the reaction conditions of the sol–gel process or even undergo an interaction with the inorganic material formed. This can be achieved, for example by the incorporation of OH-groups that interact with, for example, hydroxyl groups formed during the sol–gel process or by ionic modifications of the organic polymer.

Covalent linkages can be formed if functional groups that undergo hydrolysis and condensation reactions are covalently attached to the organic monomers.

Some typically used monomers that are applied in homo- or copolymerizations are shown in (Figure II-14).

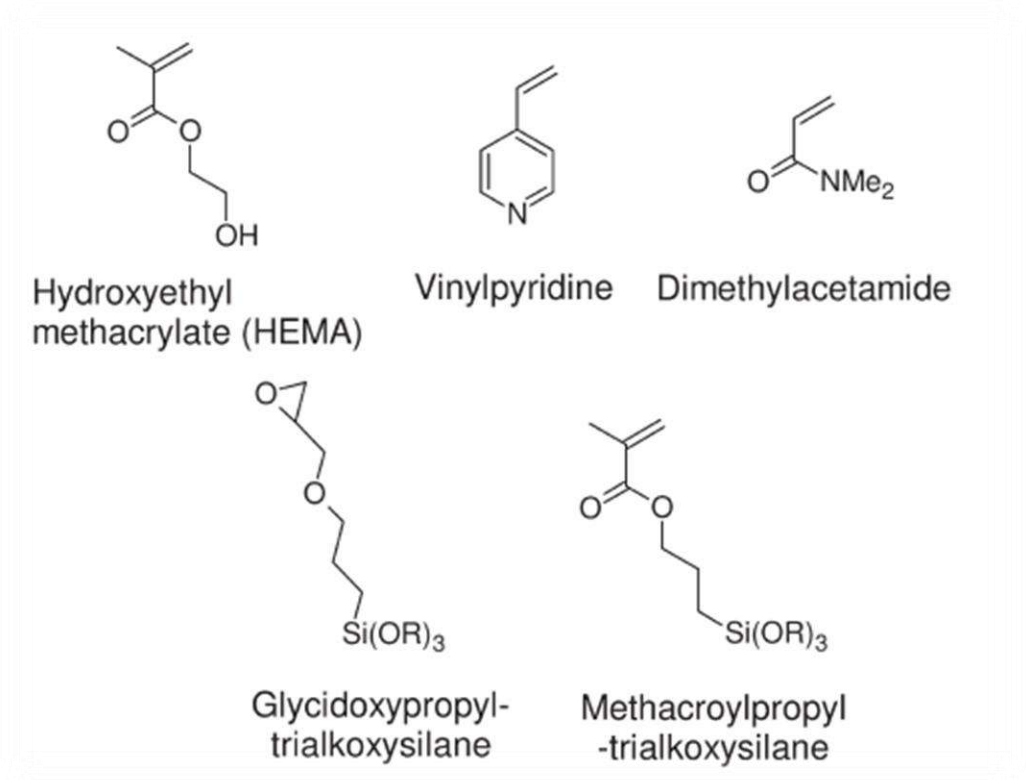


Figure II-14Organic monomers typically applied in the formation of sol–gel/organic polymer hybrid materials.

II.8.2.5 Formation of Organic Polymers in Presence of Preformed Inorganic Materials

If the organic polymerization occurs in the presence of an inorganic material to form the hybrid material one has to distinguish between several possibilities to overcome the incompatibilty of the two species. The inorganic material can either have no surface functionalization but the bare material surface; it can be modified with nonreactive organic groups (e.g. alkyl chains); or it can contain reactive surface groups such as polymerizable functionalities. Depending on these prerequisites the material can be pretreated. If the inorganic component has nonreactive organic groups attached to its surface and it can be dissolved in a monomer which is subsequently polymerized, the resulting material after the organic polymerization is a blend. In this case the inorganic components interact only weakly or not at all with the organic polymer; hence, a class I material is formed. Homogeneous materials are only obtained in this case if agglomeration of the inorganic components in the organic environment is prevented. This can be achieved if the interactions between the inorganic components and the monomers are better or at least the same as between the inorganic components. However, if no strong chemical interactions are formed, the long-term stability of a once homogeneous material is questionable because of diffusion effects in the resulting hybrid material.

In many cases intercalation of organic components into the cavities is difficult because of diffusion limits. Several porous or layered inorganic materials have already been used to prepare hybrid materials and nanocomposites. Probably the most studied materials, class in this respect is that of two-dimensional (2-D) layered inorganic materials that can intercalate organic molecules and if polymerization between the layers occurs even exfoliate, producing nanocomposites. Contrary to intercalated systems the exfoliated hybrids only contain a small weight percentage of host layers with no structural order. the formation of polymer–clay nanocomposites can be used:

1. Intercalation of monomers followed by *in situ* polymerization
2. Direct intercalation of polymer chains from solution
3. Polymer melt intercalation

Contrary to the layered materials, which are able to completely delaminate if the forces produced by the intercalated polymers overcome the attracting energy of the single layers, this is not possible in the case of the stable 3-D framework structures, such as zeolites, molecular sieves and M41S-materials. The composites obtained can be viewed as host–guest hybrid materials. There are two possible routes towards this kind of hybrid material; (a) direct threading of preformed polymer through the host channels (soluble and melting polymers) which is usually limited by the size, conformation, and diffusion behavior of the polymers and,

(b) the *in situ* polymerization in the pores and channels of the hosts. The latter is the most widely used method for the synthesis of such systems. A better uptake of the monomers by the inorganic porous materials is achieved if the pores are pre-functionalized with organic groups increasing the absorption of monomers on the concave surface. In principle this technique is similar to the increase of monomer absorption on the surface of silica nanoparticles by the surface functionalization with silane coupling agents.

II.8.2.6 Hybrid Materials by Simultaneous Formation of Both Components

Simultaneous formation of the inorganic and organic polymers can result in the most homogeneous type of interpenetrating networks. Usually the precursors for the sol–gel process are mixed with monomers for the organic polymerization and both processes are carried out at the same time with or without solvent. Applying this method, three processes are competing with each other: (a) the kinetics of the hydrolysis and condensation forming the inorganic phase, (b) the kinetics of the polymerization of the organic phase, and (c) the thermodynamics of the phase separation between the two phases.

Tailoring the kinetics of the two polymerizations in such a way that they occur simultaneously and rapidly enough, phase separation is avoided or minimized. Additional parameters such as attractive interactions between the two moieties, as described above can also be used to avoid phase separation.

One problem that also arises from the simultaneous formation of both networks is the sensitivity of many organic polymerization processes for sol–gel conditions or the composition of the materials formed.

merizations are the method of choice. This polymerization mechanism is very and can lead to very homogeneous materials. However, only selected, in particular vinyl, monomers can be used for this process.

A very clever route towards hybrid materials by the sol–gel process is the use of precursors that contain alkoxides which also can act as monomers in the organic polymerization. The released alkoxides are incorporated in the polymers as the corresponding alcohol while the sol–gel process is carried out (Figure II-15). This leads to nanocomposites with reduced shrinkage and high homogeneity.

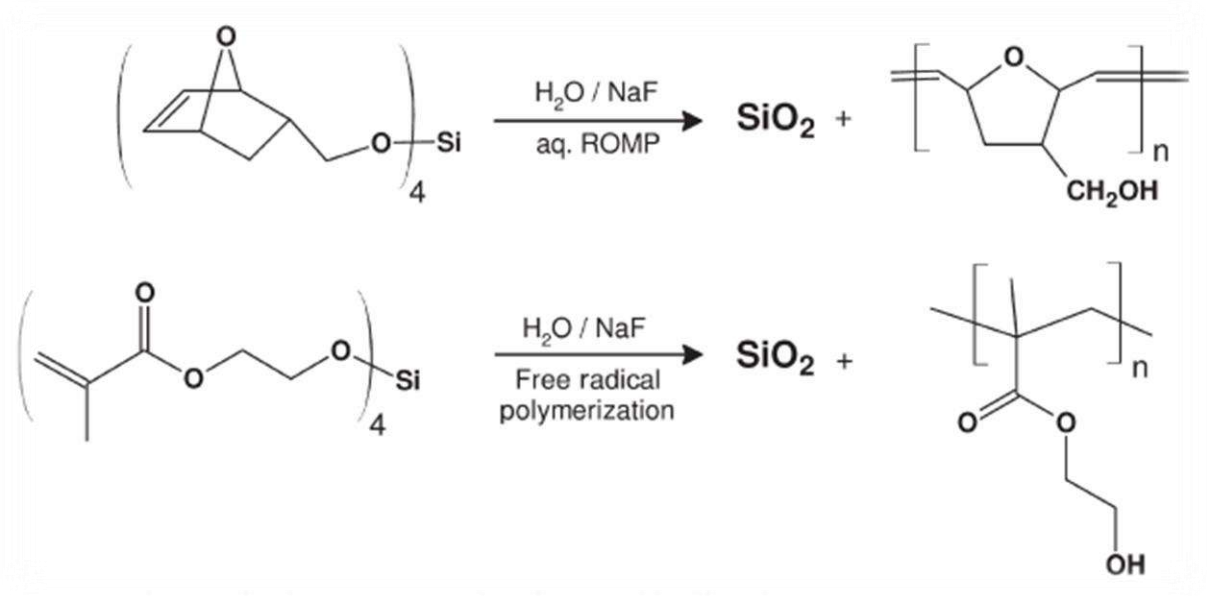


Figure II-15 Silicon sol-gel precursors with polymerizable alkoxidesf or ring opening metathesis polymerization (ROMP) or freeradical polymerization.

II.8.3 Building Block Approach

In recent years many building blocks have been synthesized and used for the preparation of hybrid materials. Chemists can design these compounds on a molecular scale with highly sophisticated methods and the resulting systems are used for the formation of functional hybrid materials. Many future applications, in particular in nanotechnology, focus on a bottom-up approach in which complex structures are hierarchically formed by these small building blocks. This idea is also one of the driving forces of the building block approach in hybrid materials.

II.8.4 Inorganic Building Blocks

Prime examples of inorganic building blocks that can keep their molecular integrity are cluster compounds of various compositions. Usually clusters are defined as agglomerates of elements that either exclusively contain pure metals or metals in mixture with other elements. Although the classical chemical understanding of a cluster includes the existence of metal–metal bonds.. Regularly pure metal clusters are not stable without surface functionalization with groups that decrease surface energy and thus avoid coalescence to larger particles. While in commonly applied metal clusters the main role of the coordinating ligands is the stabilization, they also can serve for a better compatibilization or interaction with an organic matrix. Similar mechanisms are valid for binary systems like metal

chalcogenide or multicomponent clusters. Hence, the goal in the chemical design of these systems is the preparation of clusters carrying organic surface functionalizations that tailor the interface to an organic matrix by making the inorganic core compatible and by the addition of functional groups available for certain interactions with the matrix. One major advantage of the use of clusters is that they are small enough that usual chemical analysis methods such as liquid NMR spectroscopy and single crystal X-ray diffraction can be used for their analysis. The high ratio between surface groups and volume makes it possible to get important information of the bonding situation in such systems and makes these compounds to essential models for larger, comparable systems, such as nanoparticles or surfaces.

Two methods are used for the synthesis of such surface-functionalized molecular building blocks: either the surface groups are grafted to a pre-formed cluster ("post-synthesis modification" method) or they are introduced during the cluster synthesis ("*in-situ*" method). Beside pure metal clusters and nanoparticles an interesting class of materials are metal oxides, because they have interesting magnetic and electronic properties often paired with low toxicity. Silica particles or spherosilicate clusters both have in common that the surface contains reactive oxygen groups that can be used for further functionalization (Figure II-16).

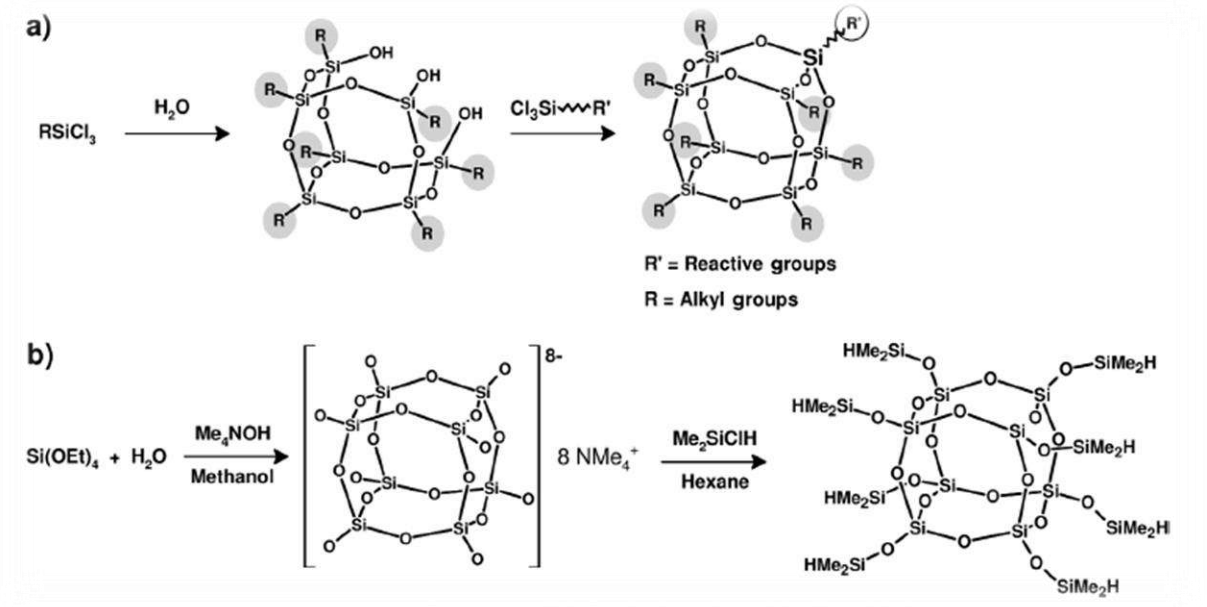


Figure II-16 Preparation of various well-defined silicon-based building blocks.

Some typical reactions lead to the attachment of initiating or polymerizable groups at the corners and therefore the resulting clusters can be used as multifunctional initiators for polymerizations or as crosslinking monomers.

Recently the modification and embedment of transition-metal oxide clusters and particles has become more and more important, because of their catalytic, magnetic or electric properties.

Two methods can be employed for such a modification: either a cluster or particle is prepared in a first step and the surface is subsequently modified, or the surface functionalization is obtained *in situ* during the preparation.

II.8.5 Post-synthetic modification

Post synthetic modification means that the cluster or nanoparticle is formed in a first step applying well-established procedures and the

functionalization with organic groups is applied in a second step. Reactive surface functionalizations are required that allow a chemical reaction with the surface decorating molecules, for example nucleophilic substitution reactions. In the case of silica-based building blocks typically surface OH-groups are reacted with so-called silane coupling agents of the general composition R4 – nSiXn (n = 1–3; R = functional or nonfunctional organic group; X = halide or OR′) to form stable covalent bonds as shown in Figure II-16. These molecules contain reactive Si—Cl or Si— OR groups that react with surface Si—OH groups to form stable Si—O—Si bonds.

A plethora of such coupling agents is commercially available, containing various organic functional groups. If the desired group is not commercially accessible, the molecule can easily be synthesized by a hydrosilation reaction. These compounds are used for the modification of silica particles or silica networks obtained in the sol–gel process. Other surface reactions can also be applied, for example the transformation of silanol groups into Si—Cl bonds followed by reactions with nucleophiles.

Prominent examples of nanoparticles that are functionalized by such methods are so-called Stöber particles which are monodispersed silica particles with Diameters between 5nm and 200nm and low particle size distributions. Similarly to spherosilicates they are formed from $Si(OR)_4$ under alkaline conditions.

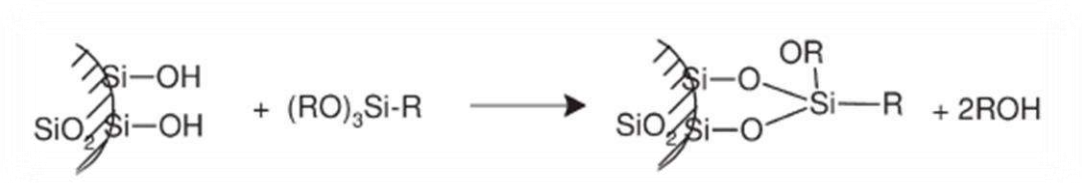


Figure II-17 typical reaction of surface silanol-groups at the surface of an silica nonparticle with a silane copling argent.

Another way to attach functional groups to the surface of a preformed building block is the exchange of surface groups similar to the above mentioned ligand exchange on gold clusters. In such a reaction, the charge and coordination number balance of the surface atoms must be retained. Electrostatic or weak coordinative bonds between surface metals and organic groups are ideally suited for this reaction type. Many stabilized metal oxide species such as titanium oxo clusters can, for example, exchange surface alkoxide groups with other alkoxides.

Beside the interaction types already mentioned, ionic interactions have also been employed for surface attachment of functional groups. Knowledge of the surface charges is necessary for this method. Charges of inorganic clusters or particles are sometimes influenced by variations of the reaction environment. Metal oxides, for example, can change their surface charge over a wide range depending on the metals and the pH value (isoelectric point).

Typical anchor groups for the interaction with such charged surfaces are carboxylates, sulfonates, phosphonates as examples for anionic groups and ammonium groups as an example for cationic groups.

A special technique for the controlled formation of hybrid materials that relates on surface charges and their interaction with counterions is the so called layer-by- Layer (LbL) deposition. It allows the formation of inorganic–organic hybrid materials using the different charges on the surfaces of inorganic and organic polyelectrolytes.

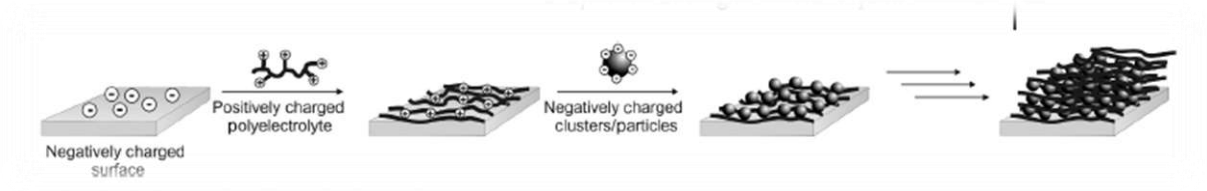


Figure II-18 Principle of layer-by-layer deposition

For example, anionic charges on a flat surface can be used to deposit cationically charged polyelectrolytes on it (Figure II-19). After deposition of the polymer the original surface charge is overcompensated and a layer of negatively charged inorganic building blocks, such as clusters or particles, can be deposited again. Afterwards again a layer of the polymer is deposited and so on. This technique enables the sequential deposition of oppositely charged building blocks. Because of its step-by-step character complex multilayer hybrid structures are readily accessible by this technique with control over layer thickness, composition and function. This method was also used for the surface functionalization of nanoparticles.

Functionalization of clusters and particles during their synthesis ("i*n situ* functionalization")

In the post-synthesis modification, functionalized building blocks are formed in two steps which are distinctly separate from each other: the inorganic core is formed first, and the functional organic groups are introduced later in a different reaction.

An alternative method is the formation of the inorganic building blocks in the presence of functional organic molecules (i.e. the functionalization of the clusters/ particles occurs *in situ*).

Silsesquioxanes with only one substitution pattern at each silicon atom are typical examples for the *in situ* formation of functionalized building blocks. As mentioned above they are prepared by the hydrolysis and condensation of trialkoxy- or trichlorosilanes, thus they contain inherently one functional group that is also present in the final material. Depending on the reaction procedure either ladderlike polymers or polyhedral silsesquioxanes (POSS) are obtained. The polyhedral compounds [RSiO3/2]n can be considered silicon oxide clusters capped by the

organic groups R.

The best investigated silsesquioxane cages are the cubic octamers, R8Si8O12. The compound [HSiO3/2]8 is, for example, prepared by hydrolysis of HSiCl3 in a benzene / cc. H2SO4 mixture or by using partially hydrated FeCl3 as the water source.

It is a valuable starting compound for organically substituted derivatives as the Si—H functions of the silsesquioxane can be converted into organofunctional groups either by hydrosilation reactions

Only a few POSS with functional organic groups are insoluble enough to be obtained directly from the corresponding RSiCl3 precursor by precipitation reactions..

The polyhedral compounds [RSiO3/2]n (POSS) or [RO—SiO3/2]n discussed so far, formed by hydrolysis and condensation of a single precursor, are models for larger silica particles covered by organic groups and prepared from RSi(OR′)3 / Si(OR′)4 mixtures.

Other bidentate ligands with polymerizable organic groups can be attached to the cluster surface by the *in situ* modification route as well (Figure II-19

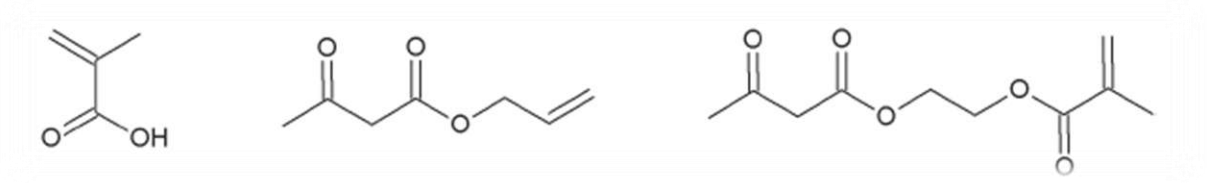


Figure II-19 Molecules that can act as bidentate ligands in the formation of surface-functionalized metal oxo clusters and metal oxide nanoparticles and which contain polymerizable groups for an attachment to an organic matrix

The head groups of these capping agents can also be other functional molecules or polymers to graft them on the surface of the inorganic nanobuilding blocks. Mercapto-terminated linear polymers were for example used for a surface functionalization which provides a much better dispersion of the inorganic nanoparticles in various organic resins.

II.8.6 Organic Building Blocks

Beside the surface-functionalized inorganic building blocks described, of course, organic building blocks can also be used for the formation of hybrid materials.

Typical examples are oligo- and polymers as well as biological active molecules like enzymes. similar principal methods have to be applied as in the formerly discussed example to increase the compatibility and the bonding between the two phases, therefore, a full description of the mechanisms is not necessary and would only lead to an enlargement of this introductory chapter. Hence, only a small selection of examples will be given here.

- Small molecules : The modification of inorganic networks with small organic molecules can be defined as the origin of hybrid materials. This is particularly true for sol–gel derived silicon-based materials. The mild conditions of the sol–gel process permit the introduction into the inorganic network of any organic molecule that consists of groups which do not interfere with these conditions. The latter is achieved by the modification of the organic molecules with hydrolysable alkoxysilane or chlorosilane groups.. In recent years functional hybrids have been the particular focus of interest. Organic dyes, nonlinear optical groups, or switchable groups are only a small selection of molecules which have already been used to prepare hybrid materials and nanocomposites.

- **Macromolecules :** Oligo- and polymers as well as other organic macromolecules often show different solubilities in specific solvents compared with their monomers; most often the solubility of the polymers is much lower than that of the monomers. Therefore, if homogeneous materials are targeted, an appropriate solvent like THF for both the inorganic and the organic macromolecules is of great benefit. Some typical monomers that form either homopolymers with a good interaction or that can be used to improve the interactions by copolymerization are shown in(Figure II-20).

A particularly interesting group of macromolecules are block copolymers, consisting of a hydrophilic and a hydrophobic segment. They can be tailored in such a way that they can react with two phases that reveal totally different chemical characters and therefore, they are known as good compatibilizers between two components.

Novel controlled polymerization methods, such as atom transfer radical polymerization (ATRP) allow the preparation of block copolymers with a plethora of functional groups and therefore novel applications will soon be available.

- **Particles and particle-like structures :** Organic colloids formed from physically or chemically crosslinked polymers can also be used as building blocks for inorganic– organic hybrid materials and nanocomposites. The good control over their properties, such as their size, the broad size range in which they can be produced, from several nanometers to micrometers, accompanied by their narrow size distribution makes them ideal building blocks for many applications. Similarly to dendrimers, special interest in these systems is achieved after their surface modification, because of their self-assembling or simply by their heterophase dispersion.

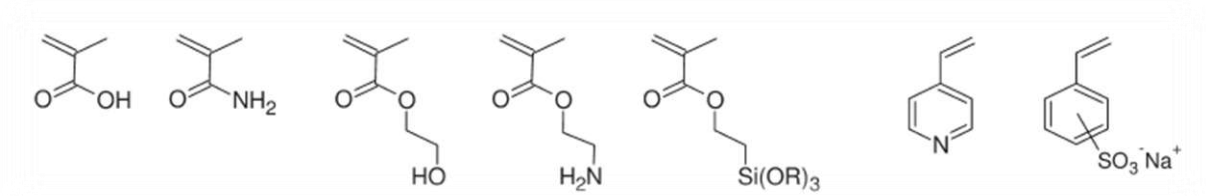


Figure II-20 Monomers that interact well with polar inorganic surfaces.

Another type of organic macromolecular building block is the hyperbranched molecules, so-called dendrimers. Dendrimers are highly branched regular 3-D monodisperse macromolecules with a tree-like structure. These macromolecules offer a wide range of unusual physical and chemical properties mainly because they have a well-defined number of peripheral functional groups that are introduced during their synthesis as well as internal cavities (guest–host systems). Spherically shaped dendrimers are, for example, ideal templates for porous structures with porosities that are determined by the radius of the dendrimeric building block. Triethoxysilyl-terminated dendrimers were, for example used as precursors for micro- and mesoporous hybrid dendrimer–silica xerogels and aerogels either as single precursors or in polycondensation reactions with tetraalkoxysilanes (Figure II-21).

The end groups of dendrimers can also be used for an interaction with metal clusters or particles and thus nanocomposites are formed often by simply mixing the two components.

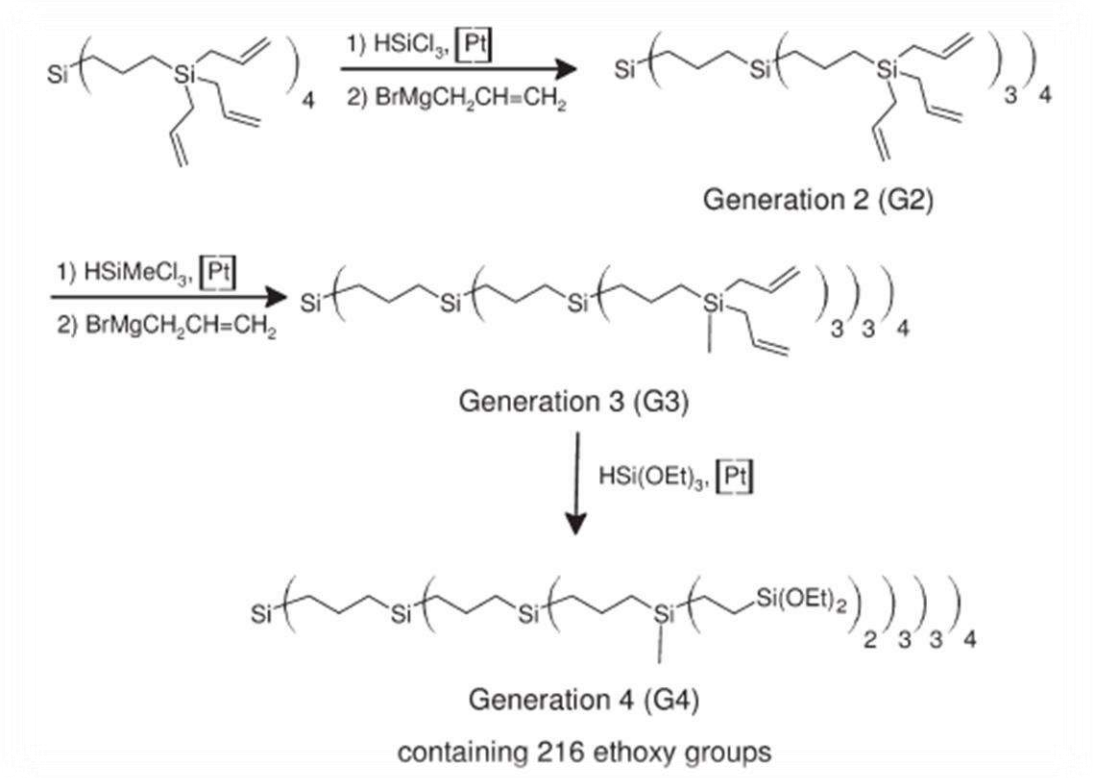


Figure II-21 Preparation of trialkoxysilyl-terminated carbosilane dendrimers.

Applying both silsesquioxanes and end-group functionalized dendrimers, both as multifunctional molecules crosslinked hybrid materials were obtained where well defined inorganic molecules acted as crosslinking components.

Beside their role as crosslinking building blocks dendrimers can form hybrid materials by themselves.

II.9 Structural Engineering and use of hybrid materials :

An important area with respect to potential applications of hybrid materials and nanocomposites is the ability to design these materials on several length scales, from the molecular to the macroscopic scale. Thin films and coatings are generally formed by dip or spin coating, fibers are formed by spinning techniques and bulk materials are usually obtained if the often liquid precursors are simply poured into forms and curing is carried out. These techniques are used for the macroscopic processing of the materials,

Applying the building block approach the structure of course is already engineered by the shape and distribution of the building blocks in the matrix. Two different techniques can be identified for a structural control on the nanometer length scale: the top-down and the bottom-up approach. The top-down approach forms the nanostructures from larger objects by physical or chemical methods and is more engineering-related, while the bottom-up approach relies on self-organization (also called self-assembly) of molecules or nanometer sized compounds.

Self-assembly is the major principle of the controlled formation of structural building blocks. It means nothing other than the spontaneous organization of unorganized systems to a complex structure, which is, first of all, an art to break and generate specific interactions and to work against entropy. There are several basic principles that have to be taken into account for a self-assembly process: the structure and shape of the building blocks, their interactions like the attractive and repulsive forces, their interactions with solvents, the environment where the reaction is carried out and diffusion processes. The balance between these principles is something which has to be set to create the desired structures.

Two principles are employed in the synthesis of hybrid materials, the self-assembly of the building blocks of the material itself and the use of templates that can self-assemble and form a shape which is applied in the preparation of a material.

Template-directed synthesis of hybrid materials : Templates can fulfill various purposes, for example they can fill space and/or direct the formation of specific structures.

Templates that fill space have been technologically used in materials processing for a long time; examples are porogenes for the formation of foamlike materials or single molecules that are employed in zeolite synthesis. In both examples the templates are removed after their use to form the pores in the materiel.

Templates for the synthesis of hybrid materials can be preformed structures such as dendrimers or nanoparticles that form 2-D or 3-D ordered structures. Furthermore, the supramolecular self-organization of single molecules into larger 2-D and 3-D structures can also be employed as a template. One example is the application of amphiphilic surfactants that organize into micelles and more complicated 3-D arrangements such as hexagonal arranged rod-like structure, cubic interpenetrating networks or lamellar structures (Figure II-22). The latter are not usually used for structural engineering because they collapse after removal of the template.

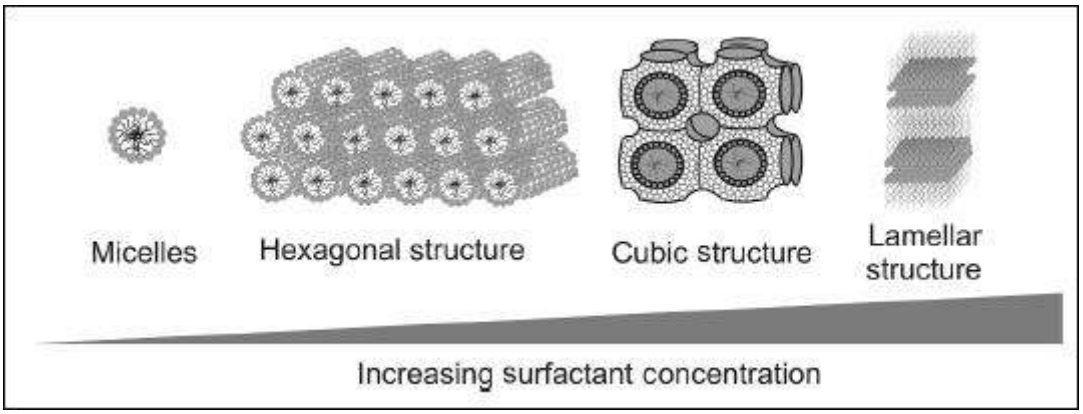


Figure II-22Examples of ordered 3-D structures obtained by supramolecular self-assembly of surfactant molecules.

The structures formed, that are dependent on parameters such as the concentration of the surfactants in the solvent, the temperature and sometimes the pH, consist of hydrophobic and hydrophilic regions and the interfaces between them which are applied in the formation of

solid materials, primarily by sol–gel process (Figure II-23). As long as the organic surfactants are still incorporated in the formed inorganic matrix the materials can be considered as inorganic–organic hybrid materials.

Colloids with narrow size distributions can order in 3-D objects so-called colloidal crystals. Most of the time latex or silica colloids are used for the preparation of such 3-D objects, because they can be prepared quite easily over different length scales and with the desired size distribution. Up to 74% the voids can be infiltrated by inorganic or organic reactive species, such as materials precursors, clusters or smaller nanoparticles and a hybrid material is formed. Generally, the templates are afterwards removed and porous materials are formed (Figure II-23).

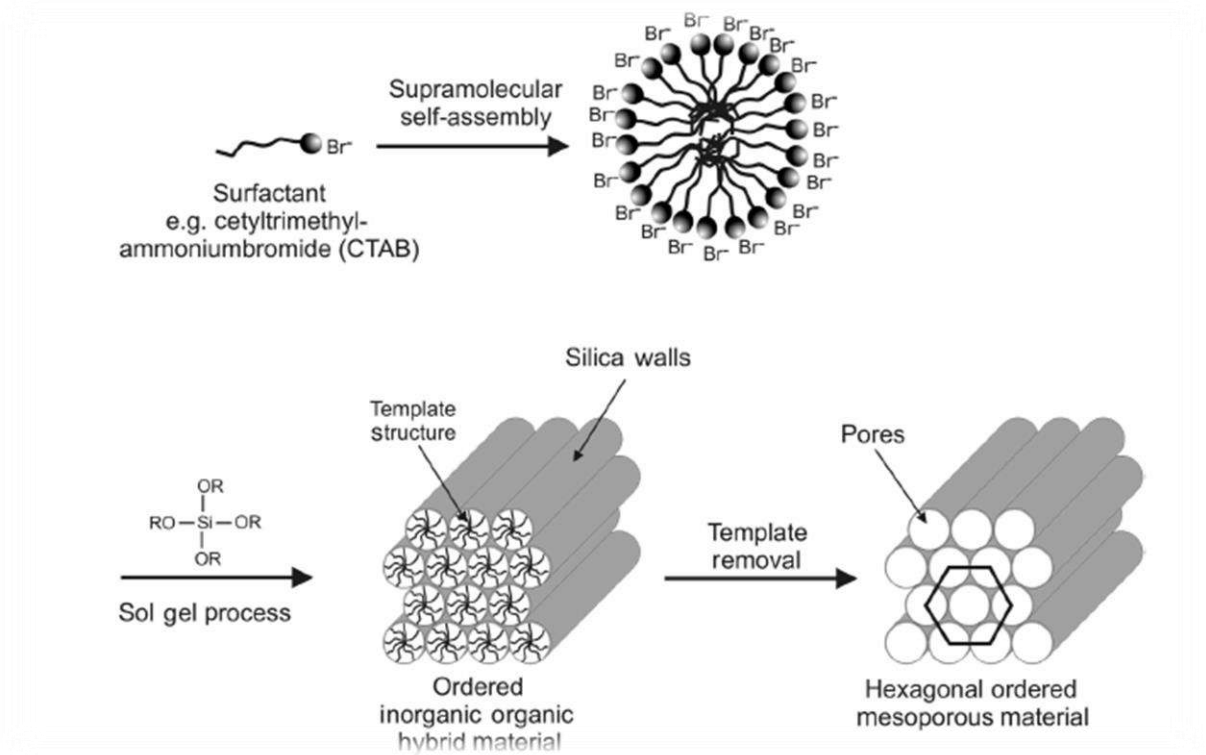


Figure II-23 Formation of well-ordered mesoporous materials by a templating approach.

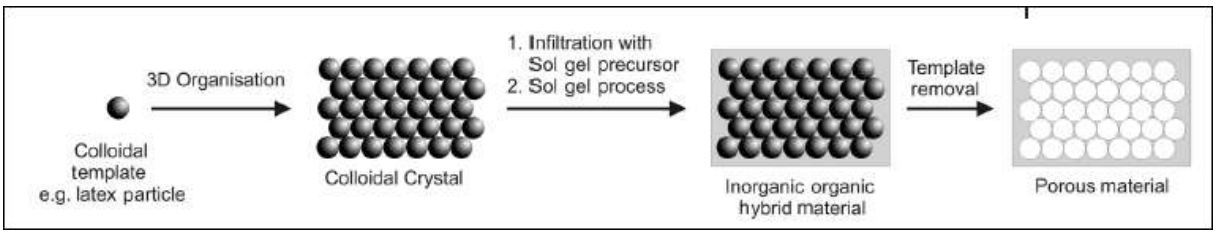


Figure II-24 colloidal crystal templating

There is almost no limit to the combinations of inorganic and organic components in the formation of hybrid materials. Therefore materials with novel composition– property relationships can be generated that have not yet been possible.

.Hybrid materials materials reveal passive optical properties, which do not change by environmental excitation, or active optical properties such as photochromic (change of color during light exposure) or electrochromic (change of color if electrical current is applied) materials. Both properties can be incorporated by building blocks with the specific properties, in many cases organic compounds, which are incorporated in a matrix.. One of the most prominent passive features of hybrid materials already used in industry are decorative coatings obtained by the embedment of organic dyes in hybrid coatings.

Another advantage of hybrid materials is the increased mechanical strength based on the inorganic structures. Scratch-resistant coatings for plastic glasses are based on this principle. Silica is preferred as the inorganic component in such applications because of its low optical loss. Other inorganic components, for example zirconia, can incorporate high refractive index properties, or titania in its rutile phase can be applied for UV absorbers. Functional organic molecules can add third order nonlinear optical (NLO) properties and conjugated polymers, conductive polymers can add interesting electrical properties. Nanocomposite based devices for electronic and optoelectronic applications include light-emitting diodes, photodiodes, solar cells, gas sensors and field effect transistors. While most of these devices can also be produced as fully organic polymer-based systems, the composites with inorganic moieties have important advantages such as the improvement of longterm stability, the improvement of electronic properties by doping with functionalized particles and the tailoring of the band gap by changing the size of the particles.

The enhancement of mechanical and thermal properties of polymers by the inclusion of inorganic moieties, especially in the form of nanocomposites, offers the possibility for these materials to substitute classical compounds based on metals or on traditional composites in the transportation industry or as fire retardant materials for construction industry.

Medical materials are also one typical application area of hybrid materials, as their mechanical properties can be tailored in combination with their biocompatibility, for example nanocomposites for dental filling materials. A high content of inorganic particles in these materials provides the necessary toughness and low shrinkage, while the organic components provide the curing properties combined with the paste-like behavior. Additional organic groups can improve the adhesion properties between the nanocomposites and the dentine.

Composite electrolyte materials for applications such as solid-state lithium batteries or supercapacitors are produced using organic–inorganic polymeric systems formed by the mixture of organic polymers and inorganic moieties prepared by sol–gel techniques..

Tithe application of hybrid composites is interesting for conducting membranes which are important for the production of fuel cells these systems because this membrane is stable at high temperatures compared with pure organic systems.

II.10 Characterization of hybrid materials

The range of characterization methods used in the analysis of the composition, the molecular and nanometer structure as well as the physical properties of hybrid materials is quite large. Many of these methods are specific for particular materials' compositions, therefore a complete list of these techniques is out of the range of this chapter. Here only a small selection of techniques often used for the investigation of hybrid materials is explained. Compared with classical inorganic materials, hybrids are often amorphous so well-established

characterization techniques such as X-ray diffraction are limited.. The heterogeneous nature of hybrid materials means that generally a variety of analytical techniques has to be used to get a satisfactory answer to structure–property relationships.

NMR techniques are a well-known powerful tool in the characterization of solutions. The advantages of NMR spectroscopy is that it is a very sensitive technique for the chemical environment of specific nuclei and a plethora of nuclei can be investigated, which makes it also an interesting technique for solid materials. However, contrary to solution NMR where spectra usually consist of a series of very sharp lines due to an averaging of all anisotropic interactions by the molecular motion in the solution, this is different for a solid sample, where very broad peaks are observed due to anisotropic or orientation-dependent interactions.

there are a variety of nuclei that can be used as probes in solid state NMR because of their NMR activity, many of them are also interesting for hybrid materials such as C, Si, Al, Sn, V, P, F and many others. By far the most investigated nucleus in the field of hybrid materials is 29Si.

29Si NMR is a powerful tool in the determination of the relative proportions of different silicon species in sol–gel derived materials.

X-ray photoelectron spectroscopy (XPS) X-ray photoelectron spectroscopy (XPS) is a surface sensitive analytical tool used to examine the chemical compositions and electronic state of the surface of a sample. The sample is placed under high vacuum and is bombarded with X-rays which penetrate into the top layer of the sample (~nm) and excite electrons (referred to as photoelectrons). The spectrum gives information on the elemental composition of the thin surface region. Shifts in the binding energies provide additional chemical information (e.g. the oxidation state of the element). The technique also offers the opportunity to use an ion bombardment to sputter the surface layer by layer and to obtain therefore a deep profile.

Electron microscopy : Electron microscopy is one of the most important techniques to characterize the materials morphology on the nanometer and nowadays even on the atomic scale. This method provides a direct image of the sample and by coupling the microscopy with analytical techniques even elemental distribution and other properties can be resolved in these dimensions.

Scanning electron microscopy (SEM) Scanning electron microscopy (SEM) produces high resolution images of a sample surface. SEM images have a characteristic 3-D appearance and are therefore useful for judging the surface structure of the sample. The electrons emitted are detected to produce an image. Beside the emitted electrons, X-rays are also produced by the interaction of electrons with the sample. These can be detected in a SEM equipped for energy dispersive X-ray (EDX) spectroscopy. Different detection modes can be applied such as the detection of backscattered electrons or the electro backscatter diffraction (EBSD) which gives crystallographic information about the sample.

Transmission electron microscopy (TEM)

In transmission electron microscopy (TEM) images are produced by focusing a beam of electrons onto a very thin specimen which is partially transmitted by those electrons and carries information about the inner structure of the specimen.

Similar to SEM further information about the sample can be obtained by analytical TEM, for example the elemental composition of the specimen can be determined by analyzing its X-ray spectrum or the energy-loss spectrum of the transmitted electrons.

Atomic force microscopy (AFM) : Atomic force microscopy (AFM) became a very important tool in the analysis of surfaces and nano objects in recent years. The method is intriguingly simple; a cantilever with a sharp tip at its end, typically composed of silicon or silicon nitride with tip sizes on the order of nanometers is brought into close proximity of a sample surface. The van der Waals force between the tip and the sample leads to a deflection of the cantilever. Typically the deflection is measured applying a laser beam, which is reflected from the top of the cantilever into an array of photodiodes..

Generally, the sample is mounted on a piezoelectric holder in all three space directions (*x* and *y* for scanning the sample, *z* for maintaining a constant force).

The resulting map of $s(x,y)$ represents the topography of the sample.

AFM technique provides a 3-D surface profile of a sample. Furthermore, samples viewed by AFM do not require any special treatment such as high vacuum and it is a non destructive techniqueAFM can only show a maximum height on the order of micrometers and a maximum area of around 100 by 100 micrometers and the scanning speed is quite low compared with SEM.

X-ray diffraction X-ray diffraction is regularly used to identify the different phases in a polycrystalline sample. Two of its most important advantages for analysis of hybrid materials are that it is fast and nondestructive. The X-ray pattern is like a fingerprint and mixtures of different crystallographic phases can be easily distinguished by comparison with reference data. Usually electronic databases such as the Inorganic Crystal Structure Database (ICSD) are employed for this comparison. The major information one gets from this method is the crystalline composition and the phase purity.

Small-angle X-ray scattering (SAXS)

SAXS is a technique where the source for the scattering of the X-rays is the inhomogeneities in the sample within the nanometer range. SAXS patterns are recorded at very low angles (typically <3–5°). In this angular range, information about the shape and size of the inhomogeneities, which can be, for example, clusters or nanoparticles in an organic matrix, and their distances is obtained. Furthermore, pores can also be defined as inhomogeneities therefore SAXS is also used to characterized regularly ordered porous materials.

Thermal analysis techniques

Thermogravimetric analysis (TGA) studies the weight changes of samples in relation to changes in temperature. TGA is commonly employed with respect to hybrid materials and nanocomposites to investigate the thermal stability (degradation temperatures), the amount of inorganic component, which usually stays until the end of the measurement due to its high thermal resistance, and the level of absorbed moisture or organic volatiles in these materials. Typically TGA plots show the weight lost in relation to the temperature and typical ranges that can be distinguished are the loss of moisture and absorbed solvents up to 150 °C, the decomposition of organic components between 300 and500°C.

Usually the measurements are carried out under air or an inert gas.

Differential scanning calorimetry (DSC) is a thermoanalytical technique that compares the difference in the amount of heat required to increase the temperature of a sample and a reference with a well-defined heat capacity measured as a function of temperature.

II.11 Summary

Hybrid materials represent one of the most fascinating developments in materials chemistry in recent years. The tremendous possibilities of combination of different properties in one material initiated an explosion of ideas about potential materials and applications. However, the basic science is sometimes still not understood, therefore investigations in this field in particular to understand the structure–property relationships are crucial.. Different building blocks and approaches can be used for their preparation and these have to be adapted to bridge the differences of inorganic and organic materials. Beside the preparation of hybrid materials, their nano- and microstructure formation, processing and analysis is important. A variety of techniques can be used for these issues.[28]

III. Mixed matrix membrane (MMM)

III.1 Introduction

Membrane technology is an attractive separation approach that has been studied extensively as a result of the fast and energy efficient process without any phase changes[29]. Membrane-based separation involves the use of membrane as a thin barrier between miscible fluids to separate a mixture. This interface may be molecularly homogeneous in which it is completely uniform in composition and structure, or it may be chemically or physically heterogeneous in which pores or layered structures are formed.

During the separation processes, a suitable force such as concentration or pressure differential is applied to allow preferential transport of one or more feed component across the membrane.

Generally, the permeation and selectivity are the two common basic performance characteristics of a membrane. In a broader context of definition, the permeability is the ability of the permeates to pass through a membrane meanwhile the ratio of permeability of the more permeable component to that of the less permeable is known as selectivity of the membrane. Higher permeability decreases the amount of membrane area required to treat a given amount of gas, thereby decreasing the capital cost of membrane units meanwhile higher selectivity will result in a higher purity gas product.

Membrane is a promising candidate for separation due to the advantages offered by the process which include high stability and efficiency, low operating cost and capital, low energy requirement and also ease of operation[30] . Furthermore, it is also known for its reliability to be used in remote locations as membrane has no moving parts and thus making it mechanically robust.

Since the last few decades, membrane-based separation has emerged as a promising process for various industrial applications, particularly in gas separation industries for air separation, hydrogen recovery and CO2 removal[31] . Other well established membrane processes in chemical and petrochemical industries are listed in Table III-1. One of the most important characteristics of membranes is the ability to control the rate of permeation of different species. The mechanism of permeation can be described using two models, i.e. solution-diffusion model and pore-flow model[32] .

Diffusion is the basis of the solution-diffusion model in which the permeable components dissolve in the membrane materials and then transport across by a concentration gradient. On the other hand gas diffusion Incomplete sentence.

The former process is of great industrial interest where it is a pressure driven process in which the vapor components pass through a non-porous membrane by a solution-diffusion mechanism. Meanwhile, gas diffusion process can be done for the microporous membranes that operate under a concentration or partial pressure gradient.

Table III-1 Various applications of membrane-based gas separation in industries.

Gas separation	applications
$O_2/_{N_2}$	Oxygen enrichment , inert gas generation
$H_2/_{hydrocarbon}$	Refinery hydrogen recovery
$H_2/_{N_2}$	Ammonia purge gas
$H_2/_{CO}$	Syngas ratio adjustment
$CO_2/_{hydrocarbon}$	Acid gas treatment, greenhouse gas capture
$H_2O/_{hydrocarbon}$	Natural gas dehydration
$H_2S/_{hydrocarbon}$	Sour gas treating
$He/_{hydrocarbon}$	Helium separation
$He/_{N_2}$	Helium recovery
$hydrocarbon/_{air}$	Hydrocarbon recovery
$H_2O/_{air}$	Air dehumidification

The successful application of membranes in an identified gas separation process, in both lab and industrial scale, greatly depends upon the selection of membrane materials with the appropriate chemical, mechanical and permeation properties. The major issue of current membrane manufacturing to researchers is to develop highly selective and permeable membrane materials which also show sufficient resistance towards the feed components as well as towards the operation condition.

Gas separation using polymeric membrane has achieved important success as high separation performance membrane since the first commercial- scale membrane gas separation system which was produced in the late 1970s. Polymeric membranes, particularly those prepared from glassy polymers, have received considerable attention because they possess advantages of mechanical properties, reproducibility and relative economical processing capability.

Polymeric membranes can be classified as: porous and nonporous membranes. A porous membrane has rigid, highly voided structure with randomly distributed, interconnected pores. Separation in these kinds of membranes is dependent on both the molecular size and pore size distribution. Non-porous membranes or dense membranes consist of a dense film in which the permeate molecules are absorbed and followed by diffusion through the membrane matrix under the driving force of a pressure, concentration, or electrical potential gradient.

The diffusivity and solubility of the permeant molecules in the membrane material play a significant role to determine the mechanism of the gas transport. Among the many

types of polymers that exhibit gas separation properties for gas mixtures, a few glassy polymers such as polysulfone (PSf), polyethersulfone (PESf), polyetherimide (PEI) and polyimide (PI) have been recognized as promising polymers with respect to their permeability and selectivity. Despite their suitability for various applications in research and commercialization, polymeric membranes are still ineffective in meeting the requirement for the current advanced membrane technology as these materials have demonstrated a trade-off between the permeability and selectivity, with an 'upper-bound' evident as proposed by Robeson.

A correlation of membrane separation data offering an analysis of the limits of polymer permeability and selectivity is often referred to as the upper boundary in which the gas separation properties of the polymeric membranes follow distinct trade-off relations where more permeable polymers are generally less selective and vice versa. The revisited upper bound relationship by Robeson for O2/N2 membrane separation for polymeric membranes is illustrated in Figure III-1[33]. Apart from that, polymeric membranes are also suffering in their limited solvent and poor chemical and thermal resistance, as well as the occurrence of swelling phenomenon that subsequently alters the membrane separation properties.

Due to the susceptibility of polymeric membranes to chemical degradation and thermal instability, their applications have been limited to separation processes where hot reactive gases are not encountered. In order to combat the inherent limitations of polymeric membrane, research is underway for alternative membrane materials. In this context, inorganic membranes that are formed from metals, ceramic or pyrolyzed carbon has attracted global interest as they offer several advantages over the polymeric membranes for many gas separations processes.

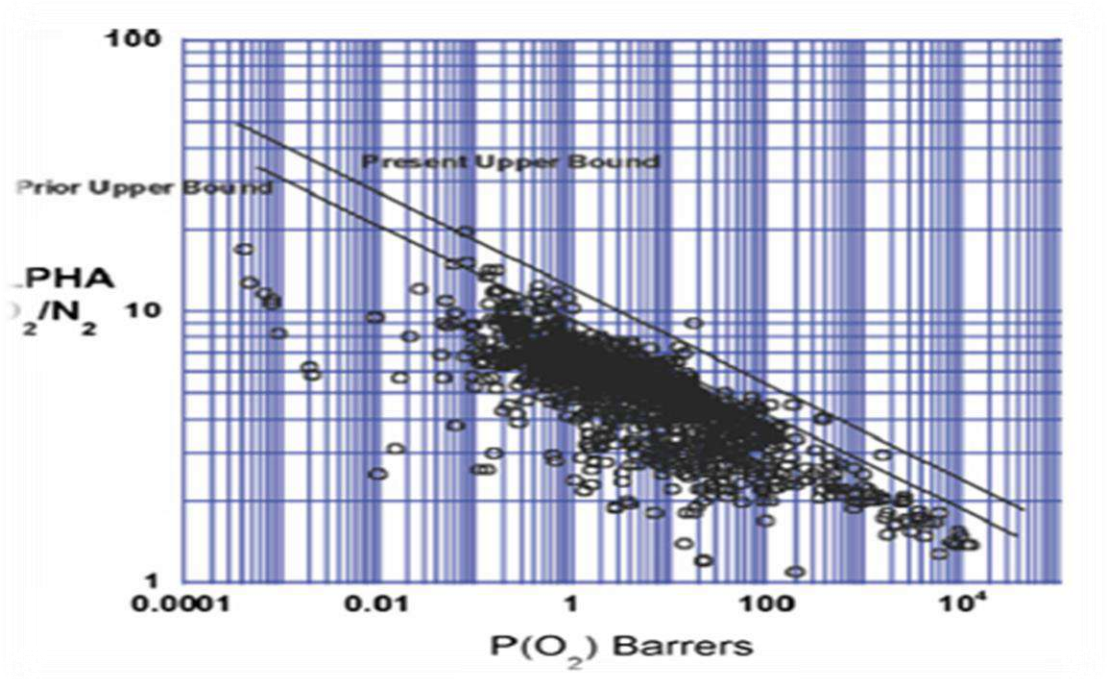


Figure III-1 Revisited upper bound data for O2/N2 membrane separation33 .

Inorganic membranes are increasingly being explored due to their attractive characteristics and advantages over the polymeric membranes. In general, inorganic

membranes can be categorized as dense and porous. Porous inorganic membranes such as zeolite and carbon molecular sieve (CMS) are favourable, rendered by their excellent selectivity which is significantly higher compared to that of polymeric membranes. Dense inorganic membranes possess very specific separation behaviours, for example metallic membranes that are hydrogen or oxygen specific. The ability to withstand high temperature for long time and the resistance to harsh operation environment have shown promise for application in membrane reactors for many industrial processes. Besides having these robust characteristics, inorganic membranes also have much higher throughput and longer life span compared to polymeric membranes.

While attracting considerable attention in many industrial processes, some disadvantages exhibited by inorganic membranes are very critical and serious to be addressed. Although some inorganic materials display properties well above the trade-off curve for polymers, such properties are challenging to duplicate in large-scale modules containing thousands of square meters of membrane areas as it involves expensive capital and repairing cost. Furthermore, the nature of inorganic membrane that is brittle and normally with low surface-to-volume ratio has also hampered the full optimisation of this material for industrial applications.

Many new attempts have been made to overcome the limitation of polymeric and inorganic membranes. Introduction of new membrane materials is still a big challenge to be researched in this frontier technology, with most researchers looking at techniques to enhance the separation processes.

So called mixed matrix membrane (MMM), where inorganic fillers are dispersed at a nanometer level in a polymer matrix have been identified to potentially provide a solution to the trade-off issues of the polymeric membrane, as well as solving the inherent brittleness problems found in inorganic membranes, is illustrated in Figure III-2. The choice of the polymer, inorganic phase and filler particle loading are some of the important parameters affecting the morphology and performance of the MMM. The successful implementation of the further development of MMM greatly lies on these parameters. In order to choose the appropriate continuous polymer phase and dispersed inorganic phase, the transport mechanisms and the gas component preferentially transporting through the membranes should be first taken into consideration.

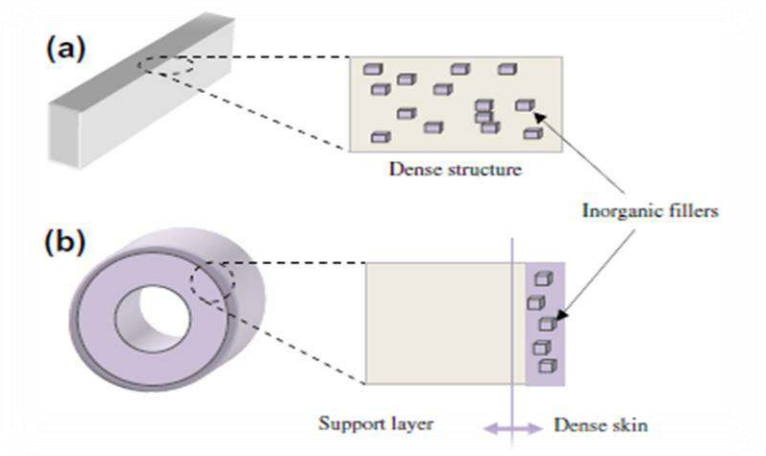


Figure III-2 Mixed matrix membranes in configuration: (a) symmetric flat dense mixed matrix membrane. (b) Asymmetric hollow fiber.

To obtain remarkably well performing MMM that surpass the intrinsic properties of the polymer matrix, the role of inorganic filler as the molecular sieve that favors one component while hindering other components to pass through it is of importance. Molecular sieves such as zeolites and CMS have been conventionally packed in the polymer phase to form a dense region of mixed matrix layers. These nanoporous materials possess the shape and size selective nature and hence allow molecular sieving discrimination by permitting smaller sized penetrates to diffuse at higher rate than that of larger sized. Recently, alternative nano-structured materials such as carbon nanotubes (CNTs), clay and metal organic framework (MOF) have also found their excellent sieving characteristic in the fabrication of MMM. However, despite the promising application of these materials as inorganic filler, the existence of adequate contact between the polymer phase and dispersed filler to eliminate the interfacial defects is always a major issue to be addressed in order to achieve the desired as well as improved performance of the resulting MMM.

The current contribution reviews recent scientific and technologically advances in the application of different types of inorganic filler materials in the fabrication of MMM. As a review of the stateof- the-art in MMM using various kinds of fillers, the progress that has already been made so far will be explored. The membrane properties, particularly gas separation performance of the MMM using both conventional and alternative materials as the inorganic phase are highlighted and discussed. This review article is meant to stimulate the interest and enthusiasm towards the currently wellidentified as well as the under exploration research on MMM among the membrane research community. Aside, it is also aimed to impart greater understanding and hence assess the effectiveness of each class of materials in tuning the intrinsic properties of the polymer phase to form a MMM with improved and desired separation performance. The conclusion and future outlook summarize the research activities and present future research directions.

III.2 Mixed matrix membrane

Since the pioneering literature by Zimmerman et al, several significant review papers on the prospects of MMM as well as the research report on the capability of MMM as alternative membrane materials for separation processes have been well published. Much research into potential new materials for gas separation membranes is driven by the limitation and disadvantages which is in existence in the current available polymeric and inorganic membranes. Few approaches have been carried out to optimize the structure of the polymer chains in order to improve the gas diffusivity by increasing the volume fraction with restrictive or selective channels communicating the voids. In addition to that, attempts have also been made to increase the solubility of permeate molecules by introducing certain chemical affinity for a gas to allow adsorption of certain moieties of the polymer. As the consequences of the efforts made, MMM, a heterogeneous membrane consisting of inorganic filler embedded in a polymer matrix, have emerged as an alternative approach in the state-of-art membrane based separation technology.

MMMs are polymer composites that involve phase separated membrane separation system. In this structurally engineered hybrid membrane, inorganic fillers act to create preferential permeation pathways for selective permeability while posing a barrier for

undesired permeation in order to improve separation performance. The superior permeability and selectivity of inorganic membranes with the processability of polymeric membranes are combined to achieve synergistic separation performance, in which the rigid adsorptive porous type inorganic phase provides superior separation properties and the polymeric phase enables the ideal membrane forming hence solving the problem of fragility inherent found in the inorganic membranes. A wide range of commercialized polymer matrix choices exist within the so-called triangular cross hatched region formed by the upper boundary such as Udel, Matrimid and Ultem have been well known for their practical applications and are readily available for the incorporation of highly selective or permeable dispersed phase to further enhance the current separation performances . The incorporation of fillers with molecular sieving properties in the polymer matrix is expected to lead to higher permeability, higher selectivity, or both compared to the polymeric membranes. The incorporation of inorganic fillers to the polymer matrix may involve (i) spherical or low aspect ratio fillers or (ii) filler thin platelets with very high ratio. The latter case is of recent interest as it offers improved separation properties over the conventional case. Although inorganic fillers are used in all cases of preparation, the resulting morphology and membrane separation performance can be varied greatly, primarily arise from different capabilities of these molecular sieves, either based on shape or size, to discriminate between different molecules present in the feed mixture.

Typically, MMMs are easy to process and manufacture as compared with the inorganic membranes. They are normally prepared by casting a solution of polymers and dispersed inorganic phase, and then evaporating the solvent in a controlled environment to obtain a dense membrane. The critical reviews on the recent development and application of MMM have revealed the viability of these materials as an alternative route for the currently existing polymeric and inorganic membranes in industrial applications. However, new fabrication approach is still in urgent need to reduce materials cost and provide greater permeability for further modifications and improvements. The significant breakthrough on MMM fabrication in useful configurations is undoubtedly essential. Besides that, the comprehensive research on MMM should also be devoted to the successful integration of the inorganic fillers to the polymeric phase.

III.3 Fabrication of MMMs

All the membranes were synthesized using the solution-casting technique. Before fabrication of membranes, the prepared MOF and polymer pellets were oven dried at 80 °C overnight to remove any trapped moisture. The dense membranes were prepared from a 5 wt% polymer solution in a water/ethanol mixture (30/70) followed by continuous stirring under reflux for 4 h at 80 °C. Afterward, the solution was cast on a Teflon substrate, and the controlled evaporation was carried out for 48 h. Further traces of residual solvent were removed by drying the membranes at 60 °C for 12 h. The resultant membrane was transparent with uniform thickness.

To fabricate MMMs, calculated amounts of MOF particles corresponding to their respective MOF loadings (10%, 20%, 30%, and 40 wt

%) were dispersed in ethanol/water solvent mixture and stirred continuously under reflux for 2 h at 90 °C. The solution vessel was then placed in an ultra-sonication bath for 0.5

h to ensure well dispersion of NOTT-300 particles. In the next step, half of the polymer pellets were added and allowed to dissolve for 4 h. The solution was sonicated again for 0.5 h, and the rest of the polymer was added. After 24 h of mixing at above-mentioned conditions, the solution was quickly cast on a Teflon substrate, and the residual solvent was dried by placing an inverted funnel for 48 h. Membranes were dried in an oven and peeled off from the substrate carefully and stored in a desiccator. Based on the MOF loading, the fabricated membranes coding is given in Table III-1.

III.4 Characterizations techniques

The crystalline features of the NOTT300 crystals were obtained by X-Ray diffraction (XRD). The diffractogram was recorded on

PANalytical X'Pert Pro DY-3805 using Cu Kα (λ=1.54 Å) radiation in the 2θ range between 5° and 50°. A TESCAN Vega3 LMU scanning electron microscopy (SEM) examined the morphology of themembranes. Membrane samples were prepared by freeze cutting under liquid nitrogen followed by a sputter coating of the gold layer using Cressington HR208 (UK) high-resolution sputter coater. Fourier transform infrared spectroscopy (FTIR) spectra were collected by a Thermo- Nicolet 6700P Spectrometer for functional group identification in the wavelength range of 4000–400 cm−1 . Gas pycnometer (G-DenPyc 2900, Gold App Instruments) was used to determine the membranes densities.

The fractional free volume (FFV) of the pure Pebax®1657 membrane was calculated by the group contribution method (GCM) as shown in

Eq. (1):

$$FFV = \frac{V - 1.3V_w}{V}$$

Where, V (cm3) is the specific volume of Pebax®1657, calculated experimentally, and Vw is the Van der Waals volume determined by GCM.

The FFV of Pebax®1657/NOTT3 00 membranes were obtained from the

Eq. (2):

$$FFV = \frac{V - \left[\frac{1.3V_W}{M}(1 - \varphi_{NOTT300})(\frac{\varphi_{NOTT300}}{\rho_{NOTT300}})\right]}{V}$$

Where, V (cm3) is the specific volume of $the\ Pebax®1657/NOTT300$[34]

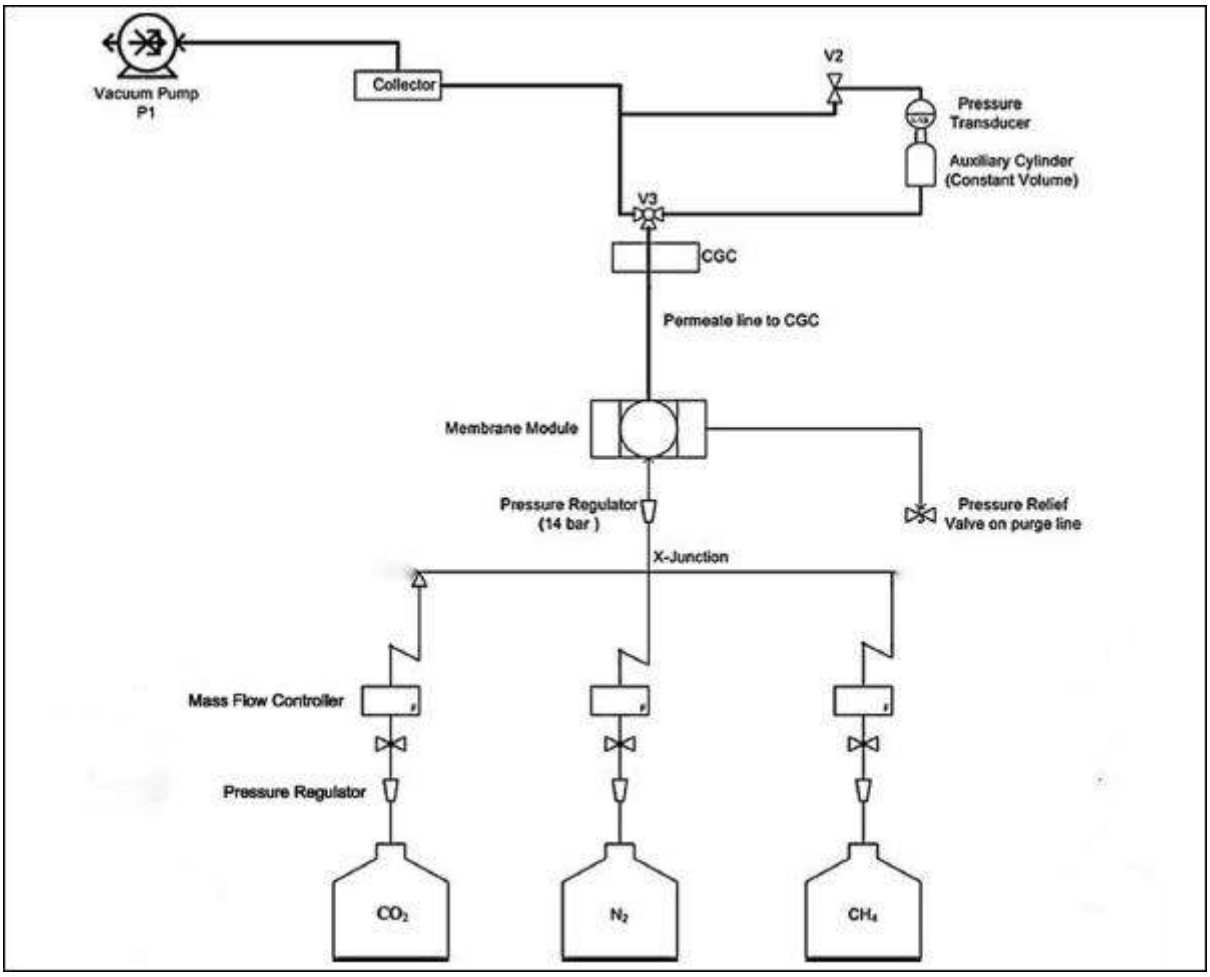


Figure III-3 Schematic diagram of the gas permeation cell.

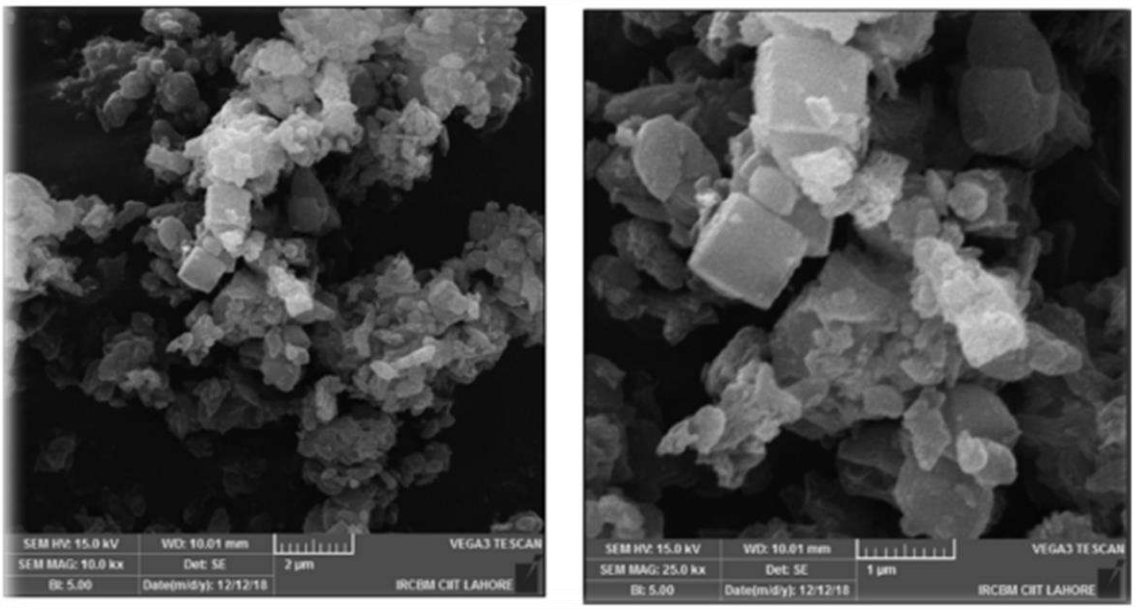


FIGURE III-4 Sem images of the nott-300 crystals

III.5 Inorganic fillers as dispersed phase in MMMs

The incorporation of inorganic fillers into polymer phase can significantly alter the transport properties of one or several gases through the MMM when compared to that of neat polymeric matrix.

The gas transport properties can be enhanced in several ways.

First, the incorporated filler particles could modify the properties of the neighbour polymer phase, which will favor the overall transport properties. This effect is especially significant for particles that are well distributed within the polymer matrix, where the fractional free volume can be greatly modified. It is also well known that the presence of filler particles may alter the packing, dynamics or conformation of polymer chain near its surface, and impart great effect on the transport of large penetrates relative to small ones. Therefore, the noticeable effect on selectivity of the gas pair involving gases with significant size difference like CO2/He can be observed. Apart from that, according to Zimmerman and Koros , the interface characteristics of the interface between the inorganic particles and the polymer matrix could determine the path to be passed through by one of the gases over the others. This characteristic allows the selective transport of certain gases hence improved selectivity is expected, or in some cases, it can also result in increased permeability by reducing the path length of the permeate molecules.

Cages with molecular dimensions open a room for separation to take place, in which the shape and size of these voids can control sorptive selectivity of the favoured permeating species. The best established example of porous materials with these sieving characteristics is the micro-scaled alumino-silicate zeolites and carbon molecular sieve that have been traditionally featured by their intrinsically high separation capacities. In fact, the formation and gas separation properties of MMM using these conventional inorganic fillers have been well documented. On the other hand, another category of nano-scaled fillers, such as silica, CNTs and layered silicate clay are normally featured by intrinsically low separation capacities. Nevertheless, a larger interfacial area between the fillers and the polymer matrix per unit volume of the fillers can be achieved and have recently attracted considerable attention due to their superior permeation properties. Generally speaking, the variation in the structures and features of these fillers may subsequently produce a difference in the separation performance behavior of the resulting MMM.

One of the main challenges encountered during the preparation of MMM is to control the chemical structure, surface chemistry as well as the particle types of the inorganic phase that would potentially affect the membrane performance. The preparation of MMM using polymer continuous phase has been reported to be complicated due to the particle agglomeration during solution preparation in which mixing techniques are necessary to break up particle agglomerates prior to the membrane processing. While glassy polymers possess a much attractive separation property relative to rubbery polymers due to their high free volume, the poor polymer chain mobility during the membrane formation may resultin a weak interaction between the filler particles and the continuous polymer phase. The interaction between the polymer and filler particles is of concern, as the undesirable channels may be created between both phases if the polymer chains do not completely interact with the filler particles. Classification, which is defined as fillers separating out from the membrane matrix due to incompatibility and forming separate filler phases or layers during the formation of

MMM may deteriorate the gas separation performance of the membranes. illustrates the void formation at the sieve-matrix interphase. The formation of these non-selective voids at the interface allows bypassing of gases hence deteriorates the selectivity of the MMM. To overcome this problem, the presence of a bridging agent to facilitate good interfacial interaction is of crucial importance (Figure III-5). In addition, approaches involving modification of surface hydrophobicity, creating surface roughness as well as the varying of particle composition and pore architecture have also been investigated. Another challenge that could be faced during the preparation of MMM is the partial blockage of the filler pore by polymer chains rendering the role of the incorporated filler.

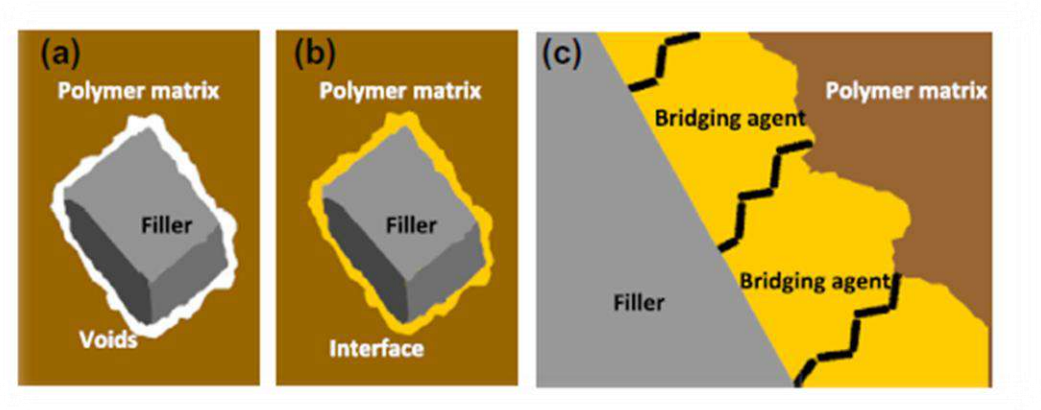


Figure III-5. Interphase properties of MMMs: (a) void formation between the phases and (b) bridging of the filler and polymer matrix upon surface modification

In order to minimize the adverse effect and to deal with the above-mentioned challenges, the well dispersion and incorporation of the inorganic particles as individuals in the polymer matrix is one of the most important tasks to be addressed. In such circumstance, surface chemistry of the particles may need to be altered using various treatment approaches.

III.5.1 Conventional fillers

Over the past decades, in order to establish MMM with higher gas separation performance relative to the neat polymeric and inorganic membranes, various inorganic materials have been explored and numerous have been identified as potential filler in membrane application. The most heavily researched type inorganic fillers are probably zeolite, CMSs (define them before abbreviation) and silica nanoparticles which have been traditionally incorporated into the polymer matrix.

These fillers are known for their versatility from the point of view of chemical composition, particle shape and possibility of chemical adaptation when embedded in polymer matrix. Particularly for

zeolite and CMS, the potentials are granted by their defined pore structure that may contribute to enhanced gas selectivity. Thus, the following sub-sections will focus on the recent development of MMM using conventional zeolite, CMS and silica, with the emphasis given to the surface modification of these fillers. The recent work on modification of the fillers and the effects of these modified fillers on polymer's segmental mobility, packing and interchain interactions as well as the gas transport properties will be discussed. Insight into

the evolutions of the recent development of MMM based on these conventional fillers offers a clear picture on how the attractive properties of the fillers can be further finetuned for excellent separation performance.

III.5.2 Zeolite

Zeolites are crystalline, hydrated aluminosilicate with opened three-dimensional framework structures, regular intracrystalline cavities and channels of molecular dimension. Zeolites possess interesting physical and chemical properties and one of the most remarkable properties, the sorption and diffusion properties of zeolite, are due to the presence of different size channels and cavities that are related to free space or void volume. . The use of zeolite in the formation of MMM as potential filler for gas separation membranes has received numerous attentions due to their thermal stability as well as their promising separation and transport properties.

Numerous numbers of reports have indicated the favorable effects of employing zeolite as the dispersed phase to improve the permeability and selectivity of various polymers for gas separation of different gas pairs. The gas transport properties of a zeolite-filled MMM rely strongly on the intrinsic properties of the zeolite particles and the dense polymer phase. The expected improvement of incorporating zeolite in the polymer matrix is gained from suspended

zeolite particles that are incorporated into the dense polymer matrix. These particles are selective for one permeate component over another. Thus, the undesired components typically travel a more tortuous path around the zeolite particles, thereby decreasing mobility for that component and hence resulted in the increase of overall selectivity for the desired species.

The proper selection on the type of zeolite is vital to obtain high performance MMM. Previous researches evidenced that the transport properties of MMM is significantly affected by the type of zeolite used with pore size ranging from 4 to 10 Å. This wide range of zeolites can separate gas components either by size discrimination or selective adsorption, depending on the sieving characteristics of the particles. As an example, zeolite 4A, is more favorable for the separation of O2/N2 gas pair than other zeolites due to its appropriate pore size of 3.8 Å to accurately discriminate between the size and shape differences of spherocylindrical O2 and N2 molecules. Figure III-6[35] depicts the predicted zeolite 4A-PI MMM performance based on Maxwell's equation where the shaded boundary represents the commercially attractive region for forming a MMM with thin selective layer.

During the early stage of the development of zeolite-MMM, incorporation of zeolite particles into rubbery polymer has shown remarkable progress in the separation performance. The compatibility between inorganic filler and rubbery polymer is good due to the high mobility of the polymeric chains capable to entirely embed the particles.

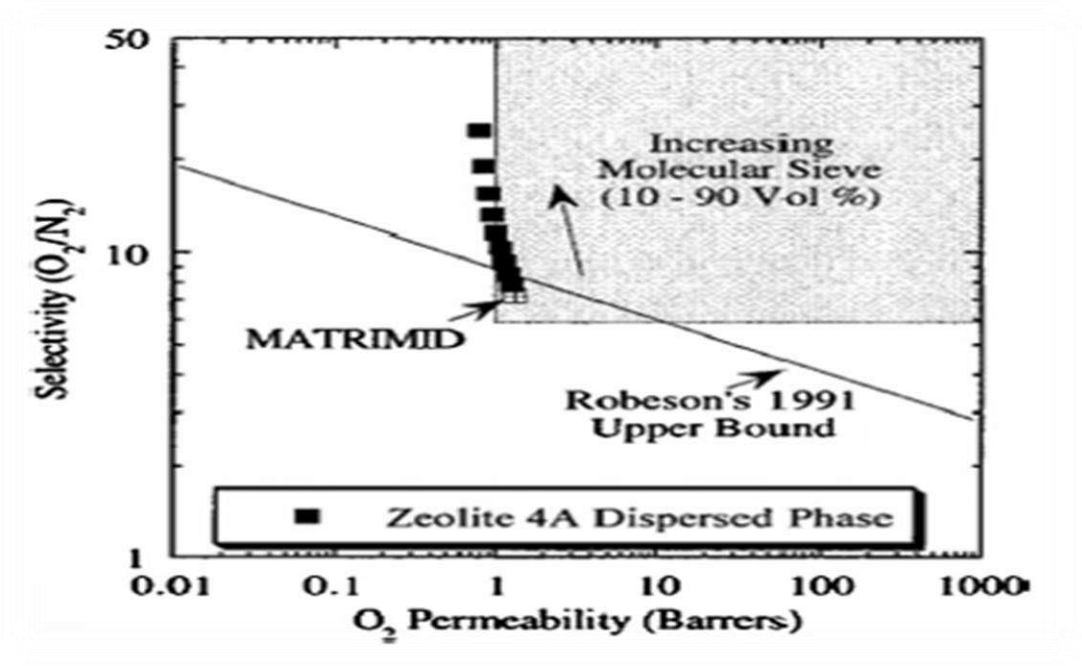


Figure III-6 Fig. 4. Predicted zeolite 4A-PI MMM performance based on Maxwell's equation.The shaded boundary represents the commercially attractive region for forming a MMM with thin selective layer38.

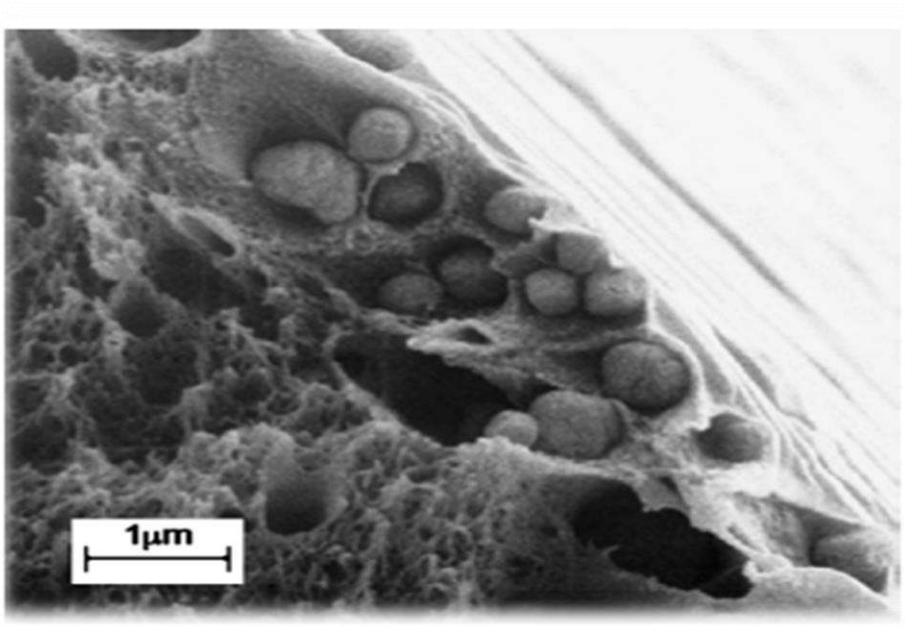


Figure III-7 Sieve-in-cage' SEM morphology exhibited by zeolite particles when incorporated in polymer matrix [36]

In the preparation of MMM, a key factor is represented by the affinity between the two phases involved in the final structure. However, unlike the good contact between rubbery

polymers and zeolites at their interfaces, initial attempts at fabricating MMM using glassy polymers and zeolites have resulted in the presence of voids between the polymer and

zeolite. Poor adhesion at the zeolite-polymer interface can result in ‘‘sieve-in-a-cage’’ morphology that is responsible for the nonselective penetration of gas molecules as depicted inFigure III-7, hence reduce the apparent selectivity of the mixed matrix membrane and increase the permeability. A wide range of modification involving the surface chemistry of zeolite fillers in the formation of MMM has been introduced to allow enhancement in polymer-filler interaction, thus optimization of the transport and separation properties.

The early attempts were made through the coating of a diluted solution of a highly permeable silicone rubber on the membrane and later on, efforts to eliminate these unselective gaps often focused on the use of a coupling agent, which is normally a low molecular weight compound with multifunctional groups, to introduce favorable interactions between the polymer and zeolite.

Low molecular weight organic compound such as TAP has been used as the tertiary component to link the polymer chain to the zeolite crystal hence promote better adhesion at the interface. Alternatively, the chain characteristics of the polymer matrix can be modified using low molecular weight additive that leads to antiplasticization of polymer matrix. Long aliphatic and polyaromatic based compounds containing polar atoms, rigid and planar structure are usually used to increase the stiffness of the polymer matrix due to reduced rate of segmental motions in the polymer chains which normally resulted in an increased selectivity accompanied with decreased gas permeabilities . Surface modification of zeolite using silanes that enables chemical link between zeolite particles and the polymer matrix is also proven to be an effective approach to improve both interfacial adhesion and gas selectivity of the MMM by modifying the surface properties of zeolite from hydrophilic to hydrophobic as well as increasing zeolite affinity to the functional groups of the polymer matrix.

summarizes the recent advances in the surface modification to improve interaction between zeolite fillers and polymer matrix.

While intensive efforts are still on-going to improve interaction with the polymer materials, the recent zeolitic development has also switched to structure and surface engineering to fabricate new kinds of molecular sieve structure with more attractive properties.

Hollow zeolite sphere (HZS), a newly developed spherical molecular sieve through layer-by-layer assembling, is of interest as it possesses advantages of zeolite as microporous and crystalline molecular sieve, as well as the properties of spherical filler that would minimize agglomeration and hence improve dispersability and interaction with the polymer phase.(my table)

III.5.3 Carbon molecular sieve

While zeolites are attracting wide attentions in the fabrication of MMM capitalizing on their size and shape selective capability, the emergence of CMS has also offered an interesting option to be potentially applied as the dispersed phase in MMM. CMS produced from the pyrolysis of polymer, primarily thermosetting polymers, are porous carbonace solids that contains relatively wide opening with constricted apertures that approach the molecular

dimensions of the diffusing gas molecules and with this manner, they are able to effectively separate the gas molecules with very similar size. Since decades ago, CMS have been evidently proven to be very effective for gas separation in adsorption application due to their superior adsorptivity for some specific gases. Thereafter, the interest in developing CMS membranes has been encouraging as a result of the outstanding permeability- selectivity combination compared to that of polymeric membranes. The high productivity accompanied with excellent separation properties that exceed the limit of trade-off boundary are mainly due to the porous nature of CMS that have promoted their viability as the selective inorganic phase in the fabrication of MMM. The utilization of CMS particles within polymer matrix is anticipated to offer several advantages over zeolites as the molecular sieve entities. One of the major benefits expected from the former combination is that CMS particles appear to have better affinity to glassy polymers, hence allow good adhesion at the interface without introducing processing complexities. Moreover, the separation performances of the CMS can be tailored by modifying the pyrolysis protocol to adapt to a specific gas separation.

The typical preparation of CMS/MMM involves the pyrolysis of polymer to obtain the CMS particles, followed by the incorporation of CMS particles in a polymer to form MMM with desired properties. The CMS incorporated Ultem and Matrimid exhibited profound improvement as much as 45% and 20% for CO2/CH4 and O2/N2 respectively, indicating that the molecular sieving pores and channels of CMS that allow for very high size and shape selectivity have without any doubt been responsible for the remarkable increase in the gas separation performance.

Few approaches have been adopted to solve the interfacial problems between the phases of CMS and polymer. Through the manipulation and control of synthesis method, CMS nanoparticles with well-defined micropores and are readily dispersed in various solvents can be produced. It has also been verified that the occurrence of the sieve-in-cage morphology can be avoided by using CMS in polymer dope with relatively high viscosities .

III.5.4 Silica

Another conventional class of inorganic filler that has received significant attention throughout the development of MMM is silica nanoparticles which can be further categorized into non-porous silica and ordered mesoporous silica. These fillers are in general introduced in the polymeric matrix to form an heterogenous membrane through sol-gel reaction in special conditions in order to develop nanoscale particles of the inorganic oxide in a polymer matrix. In this reaction, the silica precursors are hydrolyzed and condensed into the dispersed nanoparticles in the polymer matrix.

Since the dispersion is at the molecular or nano-scale level, the interactions between the silica and the organic part can be tailored in order to manipulate the morphological structure at the interface of the two phases.

The preliminary investigation of MMM incorporating silica particles, has proposed that the increased gas permeability was the result of the interaction between the residual silanol groups of the silica domain and polar gases such as CO2 hence resulting in improved gas solubility due to the increase of the Henry’s law coefficient and the Langmuir sorption constants in the MMM.

Additionally, the presence of silica particles have induced the morphology change at the interface resulting in the increased amorphous region of the MMM as well as prompting the increase in the mean distance between the polymer chains through the reduction of the polymer chain packing density at the interface between the two phases. Are shown in Figure III-8

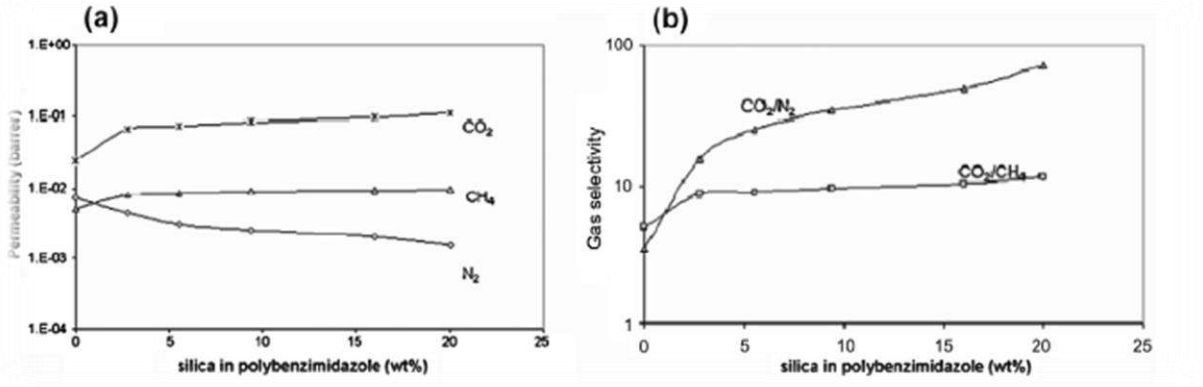


Figure III-8 The transport properties i.e. (a) permeability and (b) permselectivity of the gases through neat PBI and PBI silica hybrid membranes versus weight fraction of silica in the polymer[37].

In the consecutive study where the silica particles were chemically modified with silane coupling agent with unique bifunctional groups to create greater compatibility with the polymer matrix, they reported the reduction of the gas permeability for all gases due to the elimination of parts of the void contents. It has been suggested that by using a coupling agent, the hydroxyl groups on the surface of the silica particles could be replaced by the organofunctional groups of the coupling agent, hence facilitate better reaction with the polymer chains.

While the exploratory research on silica/polymer MMM emphasized the ability of this hybrid system in boosting the gas permeability and justified the suitability of silica particles in highly selective but low permeability polymeric membrane to result in gas separation performance that surpasses the trade off curve, recent investigations have focused on the efforts to improve both permeability and selectivity in order to make this material more attractive for industry applications.

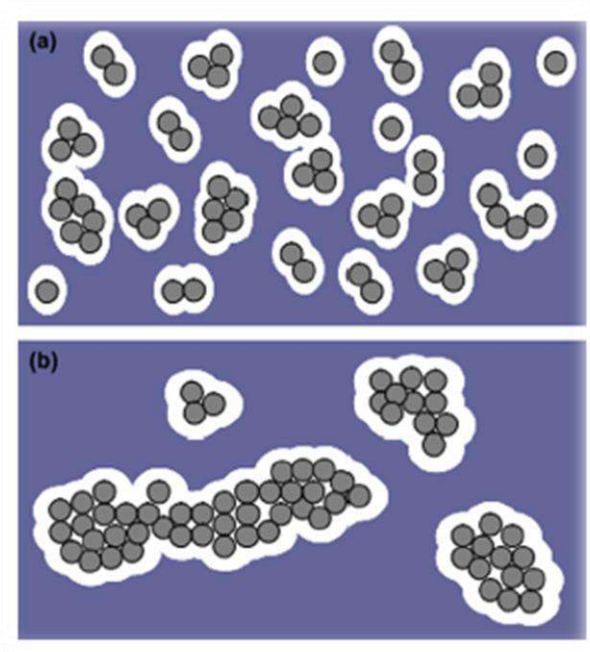


Figure III-9The possible distribution of spherical silica fillers in MMMs that are partially fused together (a) dispersed filler and voids and (b) agglomerated filler and voids[38].

Sadeghi et al. reported a simultaneous enhancement in all gas permeability and as much as 20 times increase in CO2/N2 and CO2/CH4 gas selectivity in MMM prepared by incorporating high loading of silica nanoparticles within ethylene vinyl acetate (EVA) and PBI via sol–gel method Figure III-9 shows the transport properties of gases through neat PBI and PBI-silica MMM. The relative high content of silica accompanied by the increased number of active OH group sites has given rise to an increase in solubility and a corresponding decrease in the diffusivity of the gases through the MMMs that eventually resulted in the enhanced gas solution of condensable CO2 gases in the polymer matrix and reduction in the permeability of the non-condensable N2 gas, hence changing the dominant gas permeation mechanism from the diffusion to the solution diffusion. The authors also pointed out that, the reduced diffusivity of the gases can be related to the restricted motion of the gas molecules in the polymer phase and formation of pathways with more tortuosity in the polymer upon the addition of silica particles. Very recently, Xing and Ho have investigated the separation performance of MMM prepared by incorporating fumed silica into crosslinked polyvinylalcohol– polysiloxane. The addition of silica particles has resulted in significant effect on the separation performance in which the silica content is the most influential factor to manifest simultaneously high CO2 permeability and CO2/H2 selectivity, which can be attributed to the decrease of H2 transport within the MMM as the packing density of nonporous silica increased. Ordered mesoporous silica with variety of particles size, shape and pore diameter is another form of silica that has been potentially used for the development of new generation of MMM. Prior to their employment in MMM, these mesoporous materials have already received worldwide attention as viable absorbent and membranes in many applications. Two of the most common members, MCM-41 and MCM 48 are distinguished

from their pore structure in which the former has a one-dimensional pore channel structure while the latter possesses three-dimensional interconnected cubic pore structure.4.4. Metal oxide

Metal oxide nanoparticles such as MgO and TiO2 are emerging materials due to their potential applications for membrane-based separation purposes. The primary particles with diameter in nano-scale and high specific area of these metal oxides allow improvement in particle distribution and prevent non-selective void formation in nanoparticles/polymer matrix interface. Therefore, these nanoparticles are not inherently fused together and have potential to be dispersed individually or in nanoscale aggregates. The incorporation of metal oxides normally exerts similar effect as that of impermeable silica particles in which the alteration of gas transport behaviour in such

MMM is the result of chain packing disruption and nanoscale agglomeration of nanoparticle in polymer matrix.

According to Hosseini et al. the enhanced gas permeability was ascribed to the effect of nanoparticles on the gas diffusivity due to the incorporation of highly porous MgO nanoparticles which have substituted some portions of the dense structure of polymer chains in the membrane structure. Shown in Figure III-10.

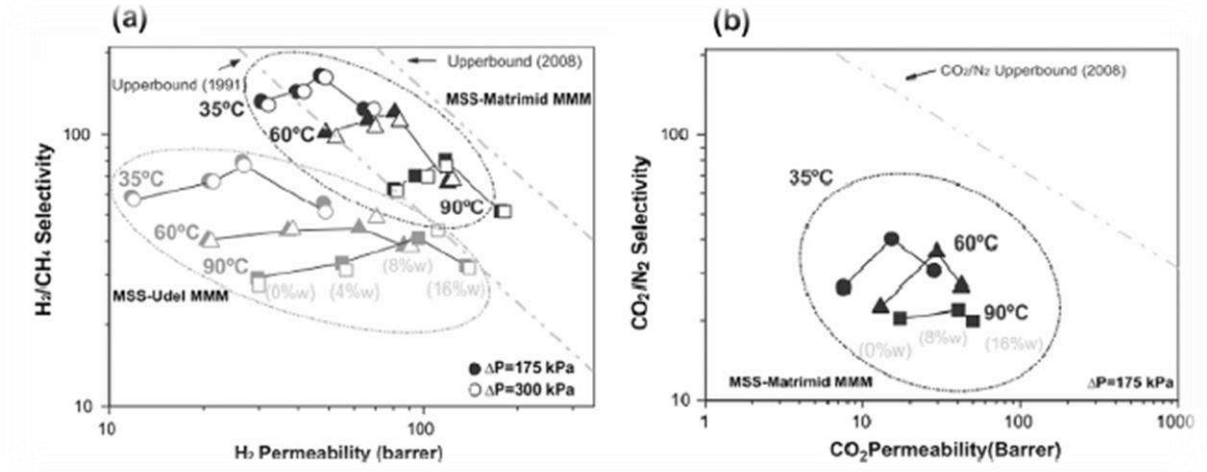


Figure III-10 Results for (a) H2/CH4 and (b) CO2/N2 at different pressures and temperatures for mesoporous silica sphere incorporated into Matrimid and Udel [39].

The increase in permeability was also seen to be the result of the presence of microvoids at the polymer–particle interface as well as the inherent transport properties of porous particles MgO nanoparticles that encompass pore size that is larger than the kinetic diameter of gases in which all the gas molecules, regardless of size, can pass through the particles without any resistance against their transport. Matheucci reported that CO2 permeability increased from 52 barrer in the neat poly(butadiene) to 650 barrer in MMM containing 27 vol% (nominal) MgO, ascribed to the surface properties of MgO nanoparticles that are basic in nature also show high affinity of physisorption towards acidic CO2 molecules hence adsorbed large concentration of CO2 even at low pressure and consequently enhanced the gas permeability.

The void formation in nanoparticles– polymer matrix interface as well as agglomeration of particles and weak interaction between polymer–nanoparticles at interface,

particularly at high loading has led to greater permeability compared to that predicted by Bruggeman's model. In general, reduction in MMMs selectivities relative to pure Matrimid has been observed, due to the decrease in diffusivity selectivity. In the case of CO2, the permeability enhancement of Matrimid containing 20 vol%

TiO2 was 2.45 times higher than neat Matrimid, while CO2/CH4 selectivity decreased by 33%, revealing that the use of TiO2 nanoparticles improved membrane performance in CO2/CH4 separation yet presented a trade-off line with relatively similar slope with respect to Robeson upper bound.

III.5.5 Alternative fillers

Despite the rapid advancement in research focusing on conventional fillers that have been traditionally applied in the preparation of MMM, the efforts to create ideal membrane with desired separation properties are still hampered by many undesired and unavoidable obstacles, as identified in the above mentioned studies. For instance, the sieving characteristic of zeolites and CMS is attractive however their size and aspect ratio is less favourable for the production of asymmetric membrane that utilizes a thin permselective layer. Furthermore, the rigid pore size with limited number of possible structure and composition in the conventionally used zeolite and CMS are insufficient to effectively discriminate the gas molecules of similar sizes.

A filler material with a controllable cage dimension is of greater interest as this feature may facilitate better sieving properties to the resulting MMM.

Nowadays, the advancement in science and technology has allowed the synthesis of nanomaterials with great control in respect to their composition. Ecentemerging materials, i.e. carbon nanotubes (CNT), clay and metal organic framework (MOF) have offered new and huge opportunities to the development of MMM endowed with attractive and desired characteristics that are comparable or even triumph over the conventional inorganic fillers.

III.5.5.1 Carbon nanotubes

In recent years there have been tremendous research advances made for carbon nanotubes (CNTs) due to their unprecedented physical and chemical properties. CNTs are a novel and interesting graphitic carbon material that is made up of graphite sheets that have been rolled into a tube. This hollow cylinder, usually capped at least at one end, is considered as nearly one-dimensional structures according to the high length to diameter ratio where the diameter of a nanotube ranges from a few to tens of nanometers, while its length can reach up to several millimeters. Generally, as depicted in Fig. 10, CNTs can be synthesized as singular tubes known as single walled carbon nanotubes (SWCNTs) or as a series of shells of different diameters spaced around a common axis called multiwalled carbon nanotubes (MWCNTs).

The initial interest of incorporating CNT in polymer lay in the possibility offered by the nanotubes to result in superb mechanical and electrical properties of the fabricated polymer nanocomposites . In the context of application in polymer composite, MWCNTs are of particular interest over SWCNTs in view of their relatively low cost and availability in larger quantities as a result of their more advanced stage in commercial production.

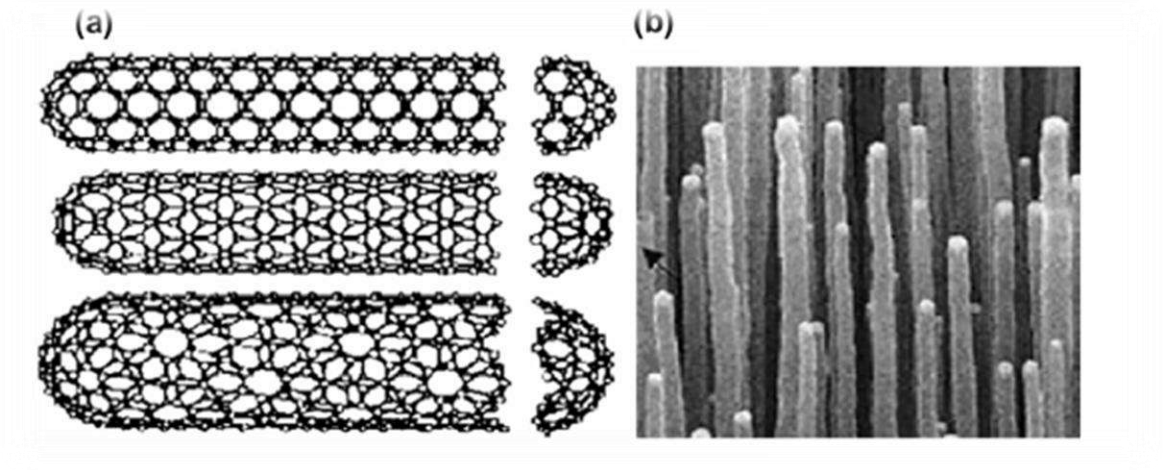


Figure III-11 Different structures of CNTs and (b) tEM of aligned CNTs .

Since the last decade, considerable research, as summarized in

My table, has been focused on the incorporation of carbon nanotubes into polymers to prepare MMM. The intensive research conducted are primarily inspired by the theoretical work by Sholl and co-workers that have reported about the transport rate of small gases such as H2 and CH4 in close packed bundles of SWCNTs being extremely rapid and in orders of magnitude faster than in zeolite and any other known inorganic nanoporous materials. The adsorption selectivity of the gas pair is strongly driven by the interaction potentials of the molecules with the graphitic CNT walls. The difference in the sorption interaction between the permeating gas molecules and CNT walls gives rise to improved separation factor of the gas pair in which it has been evidenced theoretically and experimentally that CH4 molecules showed preferential sorption capacity over other gases like H2, O2 and N2, resulting in enhanced gas selectivity .

The expected superior separation properties of the CNTs are hard to be realized due to the difficulties to assess and achieve morphological defect-free CNT/MMM in real experimental studies.

. developed MMM incorporated with 1 wt% of chitosan wrapped CNTs. A significant improvement of CO2 and CH4 permeability of 10.47 and 2.26 Barrer, respectively and increase in CO2/CH4 selectivity as much as

51% compared to neat PI were observed. The proposed transport pathway of the gases through MMMs with different cyclodextrin treated MWCNT loading is depicted in Figure III-12. At high loading, it is found that regardless of the role of cyclodextrin as the dispersing agent, the agglomeration and saturation of CNT particles in the polymer matrix hindered the fast transport of gases due to increased resistance through the nanotube cavities.

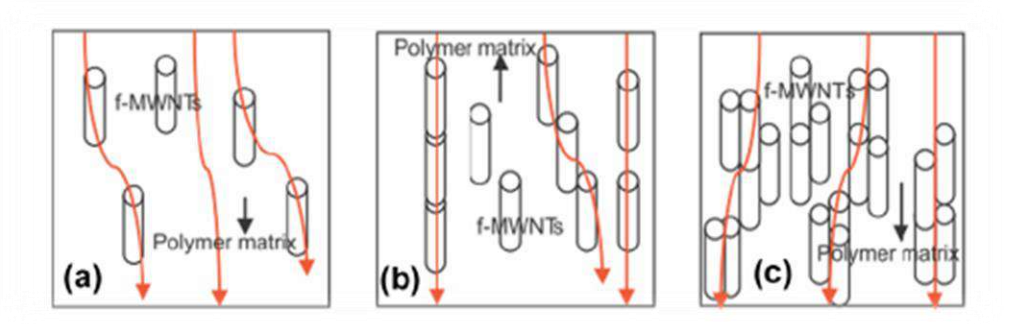


Figure III-12Proposed gas transport pathway through MMMs with different loading of MWCNTs: (a) 0.5%, (b) 0.7% and (c) 1.0%. At optimum loading of 0.7%, the oriented CNTchannels provided smooth flow and penetration of gas through the polymer matrix.

Triton X100 treated MWCNT/PEI MMM has exhibited increase in permeance of O2 and N2 as much as 88% and 120% respectively without much sacrificing the selectivity.

III.5.5.2 Layered silicate

As illustrated in Figure III-13clay is a naturally occurring layered aluminium silicate that presents itself in the form of perfectly crystalline aluminium octahedral and silica tetrahedral sheets of one to a few nanometers thick and hundreds to thousands nanometers in extent, depending on the particular layered silicate. The clay mineral, which can be further categorized into five main groups, namely smectite, illite, kaolinite, chlorite or sepiolite, is a member of the 2:1 phyllosilicates structural family, in which the central octahedral alumina sheet is sandwiched between two tetrahedral silica to form sheets that are piled in parallel to each other and are bonded by local Van der Waals and electrostatic forces.

The effort of incorporating layered silicates into polymer matrix has been known for few decades stimulated by pronounced improvement in the mechanical, dimensional, thermal, and barrier performance properties, even at very low silicate layer loading.

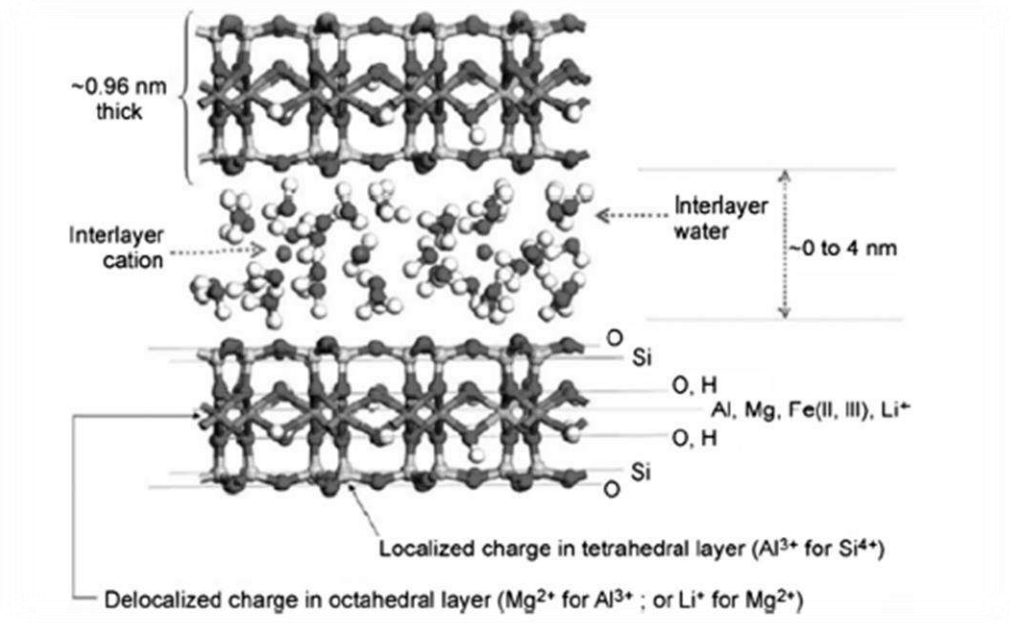


Figure III-13. Structure of layered silicates .

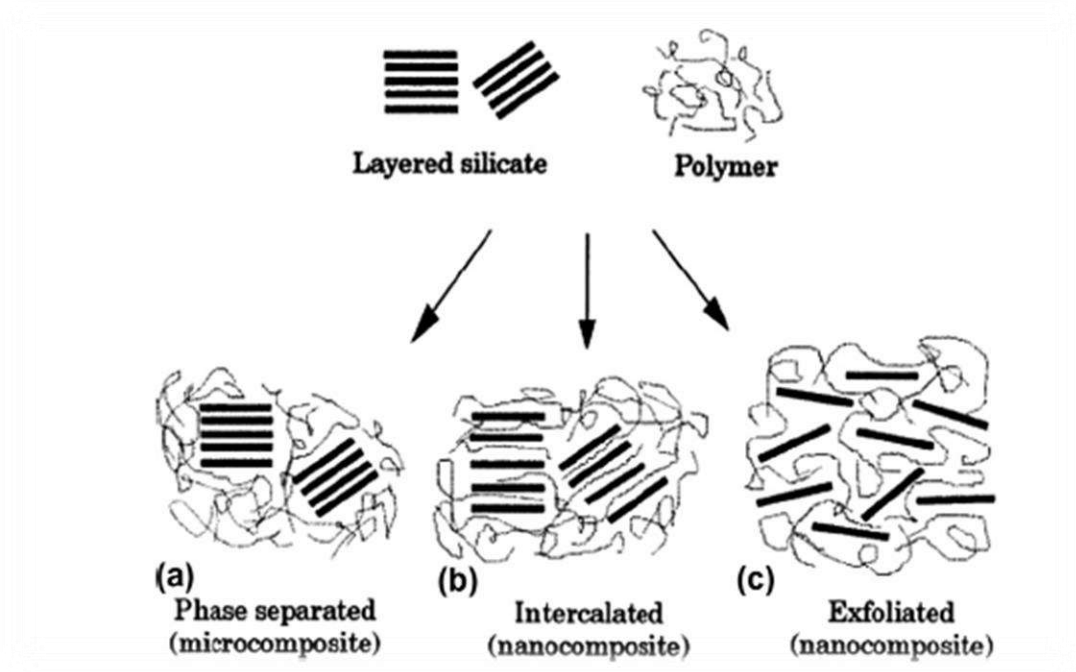


FIGURE III-14 Possible layered silicate distribution arising from the interaction of the filler and polymers: (a) phase-separated, (b) interacted and (c) exfoliated

In both cases, clay fillers are able to create a stable layer to the polymer and exhibit unique properties not seen for conventionally filled polymers.

The resulting unique properties possessed by the layered silicates render the nanocomposites ideal materials for products particularly for high-barrier packaging for food and beverage packaging Generally low oxygen permeability is required for oxygen sensitive food product, while for some food products certain amount of oxygen is required . The incorporation of layered silicate into polymer matrix exhibited remarkable molecular barrier properties as a result

One of the leading demonstrations of the gas transport properties of clay/polymer MMM has been conducted on surfactant modified Montmorillonite KSF embedded in polyamide where the increasing amounts of clay filler has induced depletion of O2 and N2 permeability but increase of the O2/N2 selectivity. This is possibly due to the barrier properties of the dispersed nanolayer in the polyamide nanocomposite membrane that resulted in a tortuous diffusion pathway for the O2 and N2.

An increased selectivity of 28% relative to the neat PEI exhibited by the clay/MMM was attributed to the high aspect ratio of clay particles combined with the intercalation due to the presence of tallow in Cloisite 15A to render an increase of tortuosity along the gas penetrant path across the dense skin layer. In another study, the authors reported the 0.5% loading of silylated-halloysite nanotubes (HCT) has resulted in the 27% CO_2 permeability increment and 8% enhancement in the CO_2/CH_4 selectivity .

III.5.5.3 Metal organic framework

Metal organic framework (MOF) MOFs are built up of inorganic sub-units in the forms of clusters, chains, layers or three dimensional arrangements that are connected to

organic linkers possessing complexing groups such as carboxylates, phosphonates, N-containing compounds by strong ionocovalent or dative bonds. MOFs can be made up from dimers, trimers, tetramers or polyhedral chains in which the linkers are readily modified with various organic groups while maintaining the same structure type in order to preserve the desired properties Figure III-15, and 14 illustrates a few commons MOFs with different structure architectures that could lead to various forms of frameworks and porosity.

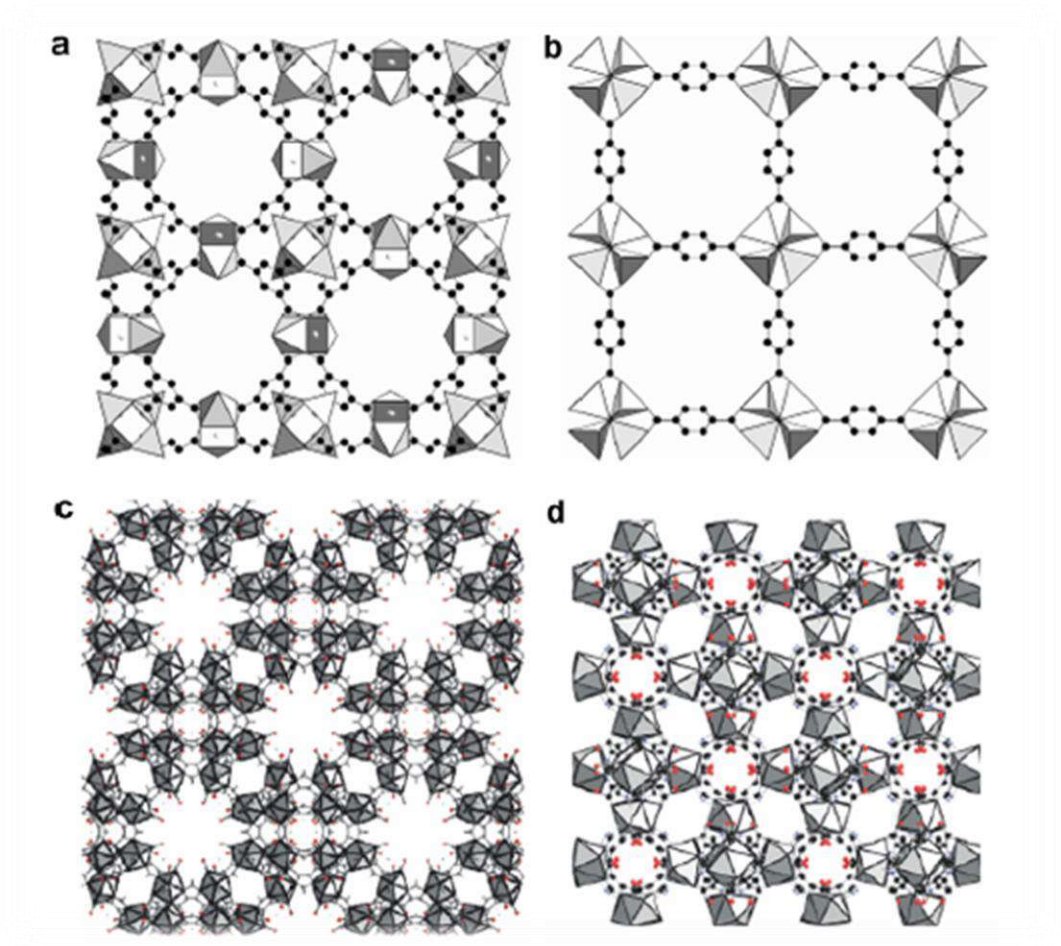


Figure III-15 Few commons MOFs with different structure architectures that could lead to various forms of frameworks and porosity: (a) HKUST-1, (b) MOF5, (c) Sodalite-ZMOF and (d) zeolite-rho ZMOF.

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MOF-5, a cubic three-dimensional structure made from Zn4O clusters linked by three 1,4-benzenedicarboxylate molecules have been assembled into a thin film membrane to promote its usage in gas applications and proven to offer unique opportunities with potential to achieve superior performance . Perez et al.Figure III-16

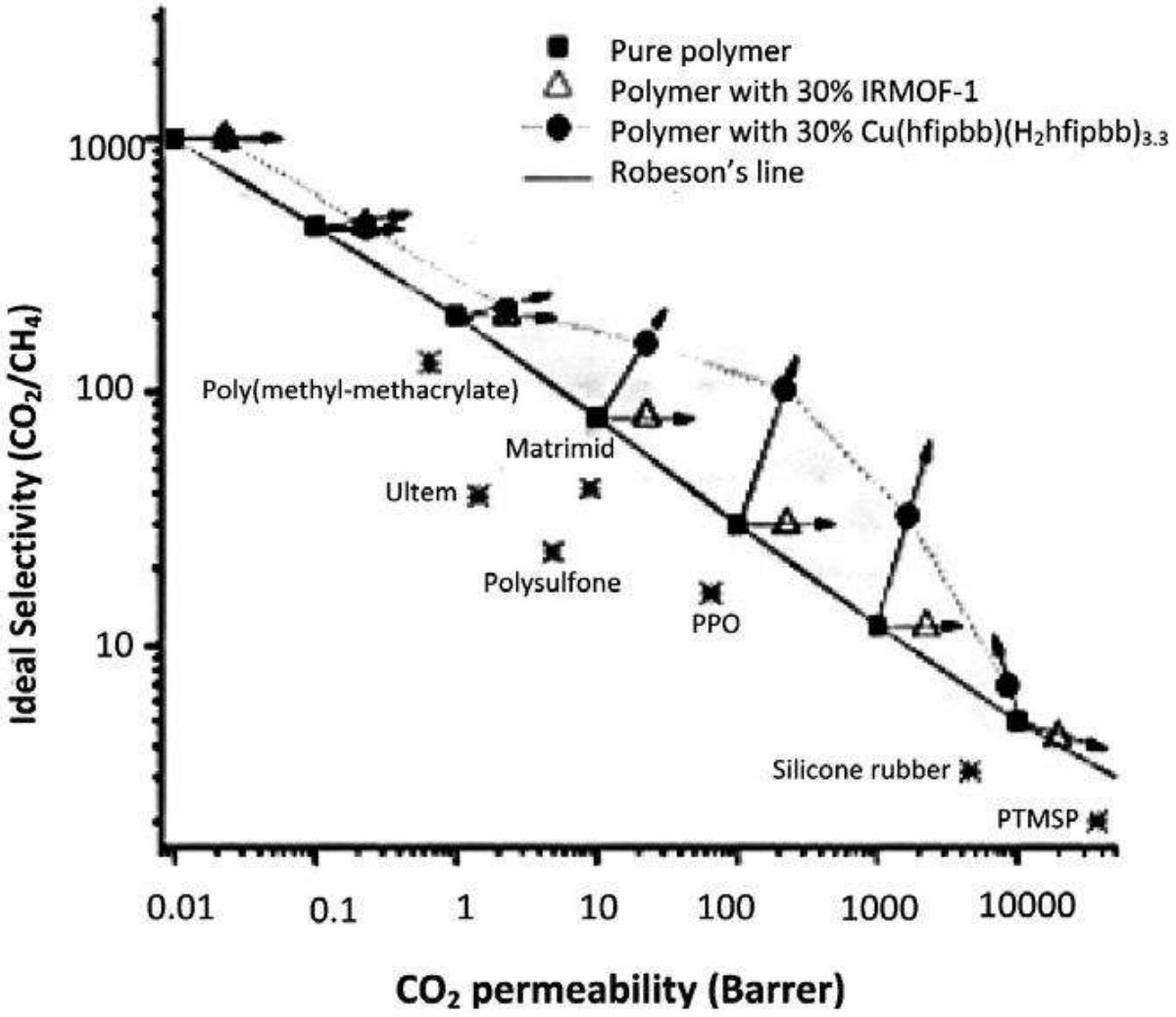


Figure III-16 Prediction of different combinations of MOF and polymer to achieve CO2/CH4 separation with high gas selectivity and permeability.

Studied the gas separation performance of MOF-5/Matrimid and observed increased permeability up to 120% while the ideal selectivity remained constant compared to that of neat polymer at 30% MOF-5 loading. Nevertheless, Matrimid incorporated with MOF-5 has exhibited a remarkable increase in selectivity for CH4 in gas mixture of CO2/CH4 and N2/CH4 due to the coupling effect of favourable MOF-5 affinity towards CH4 and larger solubility of CO2 and N2 in Matrimid. Study conducted by Ordonez et al. using ZIF-8/Matrimid MMM, significant increase in the gas permeability was observed at ZIF-8 loading lower than 50 w/w% due to the presence of MOF fillers that has increased the distance between polymer chains and disrupted chain packing in the polymer thus showing an increase in the free volume. A remarkably enhanced selectivity for gas pairs containing small gas molecules was reported at 50% ZIF loading. The increment of 213% and 290% for CO2/CH4 and H2/CH4 respectively was ascribed to the molecular sieving effect of the small pore aperture of ZIF-8 that favors the diffusion of small gas while hindering the easy diffusion of large gas molecules like CH4.

III.6 7. Conclusion and future direction

The hybrid system in MMM has the potential to address these requirements by synergistically combining the processing versatility of polymers with the separation characteristics of inorganic molecular sieves and has been the subject of numerous researches. In the last decades, the studies have asserted the unprecedented rapid growth in the field of MMM. MMM for gas separation are conventionally comprised of zeolite, CMS and silica particles embedded in polymer matrix with the ultimate goal of surpassing the Robeson trade-off boundary by overcoming the drawbacks of the existing organic and inorganic membrane materials. The past decades have witnessed an intense research effort on the application of these fillers in various kinds of glassy and rubbery polymeric materials to perform promising gas separation performance. The typical fillers that behave in this attractive manner are zeolites and CMS that have been unsurprisingly granted with tremendous attention since the first exploration of MMM in the area of membrane based separation. Nonporous silica is a class of impermeable filler that has attracted great interest rooted from their great potential to affect polymer chain packing in polymers to alter the gas separation properties. Metal oxides such as MgO and TiO2 are nanoparticles that have been studied based on their potential to be used as fillers in MMM. The interfacial region, which is a transition phase between the polymer and inorganic filler, is of particular importance to crucially determine the separation performance of the MMM. Of importance is the issues related to weak interactions between a glassy polymer matrix and inorganic molecular sieves that may lead to the formation of nonselective voids and resulting in undesired Knudsen flow. Therefore, instead of seeking perfect matching of the inorganic fillers and polymer matrix to battle the weakness of MMM in term of adhesion and interaction between the two phases as broadly focused during the early studies, recent efforts have pinpointed the necessity to modify the surface of fillers to enhance the interfacial properties

MMM consist of inorganic fillers incorporated into a polymer matrix have the potential to extend or even surpass the separation benefits exhibited by the polymeric membrane platform. The unique behaviour found in this hybrid system will allow us to apply it in new and different applications. Further understanding of the fundamentals of this material, including structure and dynamics, will allow us to produce materials avoiding the trade-offs of conventional systems. Hybrid materials with organic–inorganic or bio–inorganic character represent not only a new field of basic research but also, via their remarkable new properties and multifunctional nature, offer great prospects for many new applications in extremely diverse fields.

III.7 Gas separation in MMMs :

The first incentive for creating hybrid organic-inorganic membranes was an increase in the gas separation performance of existing mesoporous metal oxide or glass. Grafting introduced gas transport mechanisms other than the low-selective Knudsen diffusion of the mesoporous supports. Both silanation and phosphonic acid grafting using primarily apolar long alkyl or perfluoroalkyl groups were applied for this purpose. Depending on the groups grafted, surface diffusion or solubility of a particular gas could be enhanced. The research in the 1990s resulted in an only modest selectivity increase.

Permeability (P) is the ability of a molecule to pass through a solid medium (i.e. polymer). Permeability is the measurement over time of the quantity of a species that crosses through a polymer film subjected to a difference in concentration of the species considered.

The first law of Fick is the most commonly used equation to describe the transport of a gas through a polymer film in the ideal case (simple and non-plasticizing gases). The specific flow J of the permeating gas is equal to:

$$J = -D\frac{\partial C}{\partial x} \quad \text{(1)}$$

With

D: the diffusion coefficient (or diffusivity) of the gas ($m^2.s^{-1}$); C: the concentration of gas in the membrane ($mol.m^{-3}$) and x: the thickness of the film (m)

If we consider a linear relationship between the gas pressure and its concentration at the interface (Henry's Law), the following equation applies:

$$P = s \times c \quad \text{(2)}$$

S: solubility of the gas in the polymer film ($mol.m^{-3}.Pa^{-1}$)

P: gas pressure in the polymer film (Pa)

Assuming that S and D are independent of gas concentration, the integration of the law of Fick over the entire thickness of the polymer film gives the expression of the specific flow of gas J through the film:

$$J = D \times S\frac{\Delta P}{\mathrm{d}} \quad \text{(3)}$$

The capacity of a film to transport a gas is described by the permeability coefficient Pe defined by:

$$Pe = D \times S = \frac{Qte\ permeant \times thickness\ film}{\text{area film} \times \Delta p_{\text{preament}}^{x/y}} \quad \text{(4)}$$

And x/y = upstream / downstream.

Pe is expressed in $mol.m^{-1}.s^{-1}.Pa^{-1}$. However according to the applications of many other units are used.

The coefficient of permeability P_e is an intrinsic property of the polymeric material. It is independent of film thickness and upstream / downstream pressure difference (driving force). (5)

The diffusion coefficient D (in $m^2.s^{-1}$) is the kinetic parameter of global transport. As we have seen, it describes the mobility of the penetrant in the membrane and depends mainly the size of the penetrant molecule, movements of the segments of polymer chains and free volume thereof. (5)

The solubility coefficient S is the thermodynamic magnitude of the overall transport. He represents the amount of dissolved gas molecules in the membrane under the conditions balance. It is related to the gas / polymer interactions and the free volume of the membrane. (5)

The coefficient of permeability P_e generally follows the Arrhenius law:

$$Pe = P0exp^{(-EP/RT} \quad \text{(5)}$$

With

P_0: pre-exponential permeability factor equal to D0.SO ($mol.m^{-1}.s^{-1}.Pa^{-1}$)

E_p: activation energy of global transport.

A: The perfect gas constant ($J \cdot mol^{-1} \cdot K^{-1}$)

Several other quantities are also used to characterize the passage of gas through a movie:

Permeation rate: This is the coefficient of permeability without take into account the difference in pressure.

$$Permeation\ rate = \frac{Permeant\ quantity \times Thickness\ film}{Area.Time} \quad \text{.....(6)}$$

Permeation: This is the coefficient of permeability regardless of the thickness of the movie. When the thickness of the film is unknown, we prefer to use permeance rather that permeability.

$$permeance = \frac{Qte\ permeant \times thicknessfilm}{Area \times Time \times \Delta P_{permeant}^{x/y}} \quad \text{..... (7)}$$

The flow of gas: when it comes to oxygen the flow is noted OTR (Oxygen Transmission)

$$OTQ = \frac{Qte\ permeant}{Area.Time} \quad \text{..... (8)}$$

The permeability of the polymers to different gases generally ranks, depending on the nature of the permeant, in an order that is only slightly influenced by the chemical nature of the material. In other words, there are two categories of gas: fast gases and slow gases. The first category gathers, on the one hand, the gases which have a high mobility (i.e He and H2), and on the other hand, the gases whose polar character makes them soluble in polymers. The category of slow gases concerns gases that are both poorly soluble and not very mobile, it generally includes molecules that are devoid of dipole moment and have a diameter greater than 3 Å: O2, N2, CH4 gases and most of the polyatomic molecules are part of this category.

IV. STUDY OF THE PERMSELECTIVITY OF MIXED MATRIX MEMBRANE

IV.1 Introduction

The aim of the work is to elaborate a permeability data for different types of Mixed Matrix Membranes to extend a previous available data on polymers gas permeability available in Material and Environmental Laboratory of Medea university. This work leads to find the best membrane in terms of performance in gas separation.

MMMs consist of frame and filler, and selection of these both parts is important and influences the morphology and membrane performance of the mixed matrix. The membrane of the mixed matrix can be polymeric, zeolite, ZIF, MOFs, CMS…

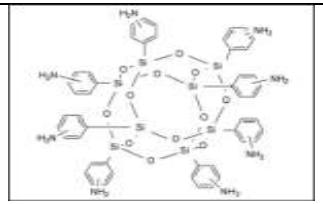
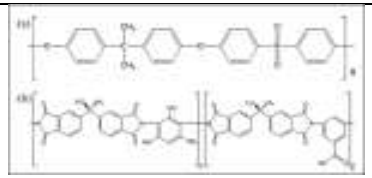
Gas separation using polymeric membrane has achieved important success as a high separation performance membrane; Among the many types of the polymers that exhibit gas separation properties for gas mixture, a few glassy polymers such as (PFS), (PESF), (PE) and (PI) have been recognized as promising polymers with respect to their permeability and selectivity , but to obtain remarkably well performing MMMs surpass the intrinsic properties of the matrix, the role of inorganic filler as the molecular sieve that favors one components while hindering other components to pass through it is of importance such as molecular sieve such as zeolite, CMS, CNTs, MOFs….

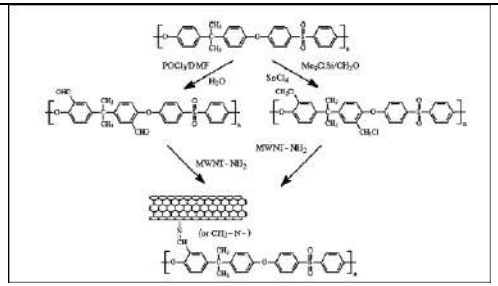
The first part of this work is devoted to the collection of permeability data from the bibliography concerning various types of MMMs.The second part, which constitutes the bulk of this work, is devoted to compare MMMs permselective performance for separation of two gas pairs CO_2/N_2 and CO_2/CH_4).

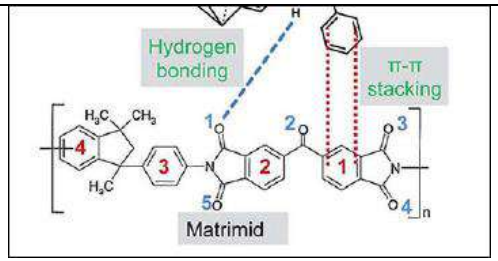
IV.2 Data collection

To prepare this database, we collected, in the first step, publications on mixed matrix membranes and their corresponding matrix polymeric membranes. In the second step, we have selected only the membranes used to separate the gas and contain permeability data about the separation of the two gas systems CO_2 / N_2 and CO_2 / CH_4. Hence, we have in final kept 38 families of the mixed matrix membranes which are resumed in Table IV-1. This table contains also condition.

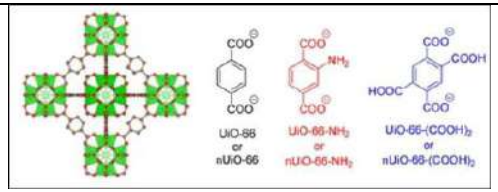
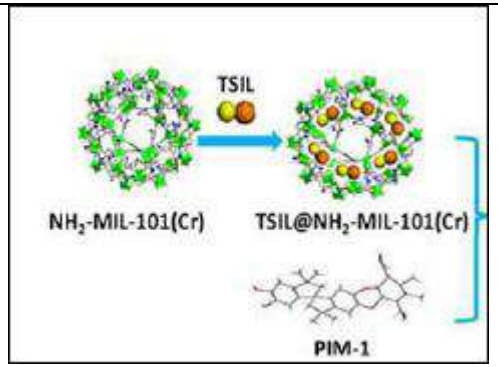
Table IV-1MMMs gas separation performance (permeability of CO_2 and selectivity of CO_2/N_2 and CO_2/CH_4)

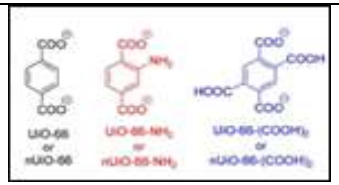
N	MOTIF	STRECTURE	Filler (wt.%)	PERMIAPILITY en barrer			Sélectivité		T en °c	P en atm	reference
				CO_2	N_2	CH_4	$\frac{co_2}{N_2}$	$\frac{co_2}{CH_4}$			
1	6FDA-MDA/OAPS		0 5 10 20	16.30 16.40 16.50 15	- - - -	0.39 0.37 0.31 0.23	- - - -	41.00 44.00 53.00 63.00	35	10	[40]
2	PSF/MCM-48		0 10 20	4.46 8.46 18.21	- - -	0.16 0.33 0.76	- - -	26.23 25.61 23.65	35	4	[41]

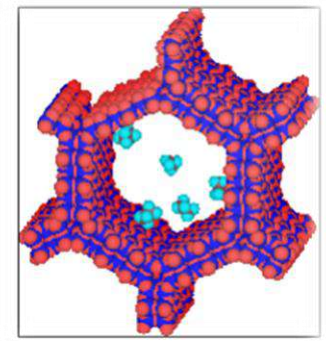
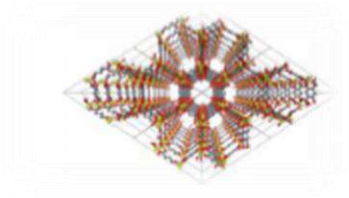
3	PSF/SWNT		0 5 10 15	3.90 5.12 5.19 4.52	- - - -	0.17 0.27 0.28 0.28	- - - -	22.94 18.96 18.53 16.14	35	4	[42]
4	PDMS-41/CNT		0 2 10	166.02 190.67 191.30	- - -	28.18 34.17 36.71	- - -	5.89 5.58 5.21	35	4	[43]
5	Matrimid®/MOF-5		0 10 20 30	9.00 11.01 13.80 20.20	- - - -	0.21 0.20 0.33 0.44	- - - -	41.70 53.63 40.59 44.89	35	2	[44]
6	Matrimid®/Meso-ZSM-5		0 10 20 30	7.29 8.27 8.65 14.61	- - - -	0.21 0.12 0.13 0.25	- - - -	34.71 67.19 40.59 44.89	-	1	[45]

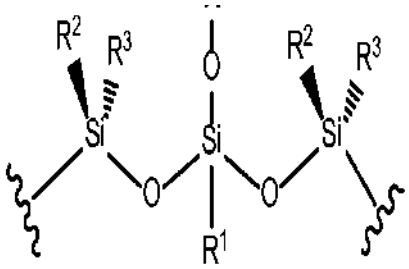
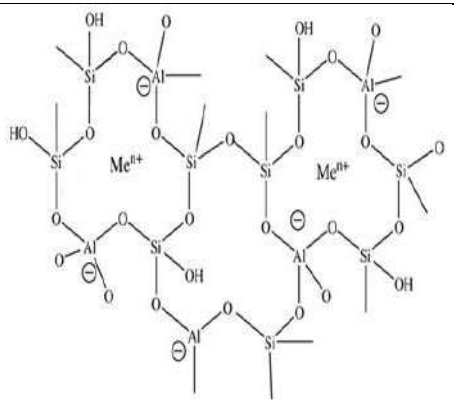
7	Matrimid®/Cu–BPY–HFS		0 10 20 30 40	7.29 7.81 9.88 10.36 15.06	- - - - -	0.21 0.24 0.35 0.37 0.58	- - - - -	34.71 31.93 27.62 27.45 25.58	35	1	[46]
8	6FDA6FpDADABA/ZSM-2		0 20	21.97 15.96	- -	0.72 0.66	- - -	21.97 15.96	35	1	[47]
9	Matrimid®/C60		0 2.5 5 10	7.15 5.00 4.54 3.79	- - - -	0.19 0.13 0.12 0.10	- - - -	36.00 37.72 35.75 34.77	Amb	1	[48]
10	PC (7%)/ECPPY		10 15 20	7.65 7.53 7.39	- - -	3.17 2.70 1.59	- - -	2.41 2.78 4.52	50	1	[49]

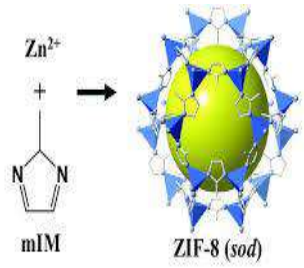
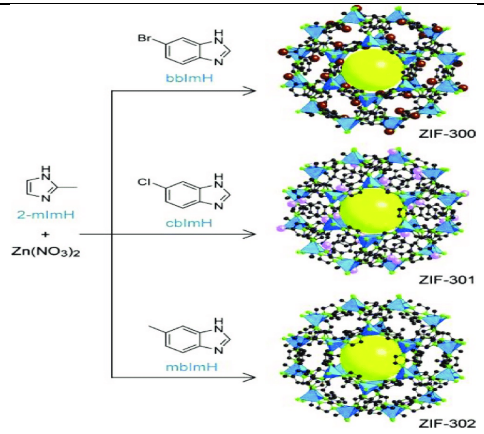
			25 30	12.12 19.87	- -	3.19 14.5	- -	3.79 1.37			
11	PC (9%)/ECPPY		10 15 20 25	7.79 7.64 7.55 19.1	- - - -	22.9 2.85 1.75 14.92	- - - -	2.34 2.68 4.29 1.30	50	1	49
12	PC (7%)/CPPY		10 15 20	4.10 4.50 5.20	- - -	0.25 0.26 0.30	- - -	16.4 16.67 17.33	50	1	49
13	Matrimid® 5218/CMS 800-2		0vol% 17vol% 19vol% 33vol% 36vol%	10.00 10.30 10.60 11.50 12.60	- - - - -	0.28 0.23 0.22 0.24 0.24	- - - - -	35.30 44.78 46.09 47.95 52.50	35	3.5	[50]
14	Ultem® 1000/CMS 800-2		0vol%	1.45	-	0.033	-	43.00	35	3.5	50

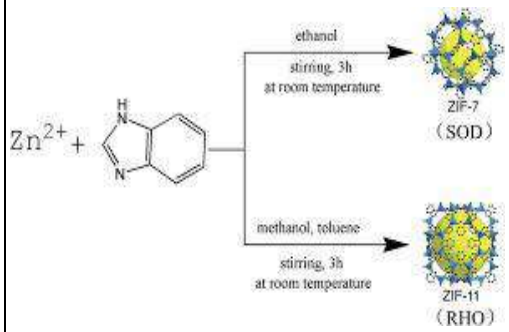
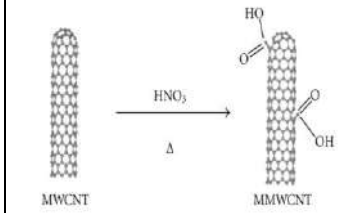
			16vol% 20vol% 35vol%	2.51 2.90 4.44	- - -	0.058 0.018 0.086	- - -	43.26 48.33 53.98			
15	Polymer of intrinsic microporosity (PIM-1) NH2-UiO-66		20	12.498	0.39	0.23	31.9	54.2	25	1.79	[51]
16	6FDA-Durene Polymide 5 wt. %. CNT-MIL		50	818	-	27.54	-	19.7	25	1.97	[52]
17	PIM-1 TSIL-modified NH2-MIL-101(Cr)		5	2.979	0.08	-	37.0	-	25	2.96	[53]
18	Pebax ZIF-8 @GO		6	249	5.29	-	47.0	-	25	0.98	[54]
19	Ethyl cellulose ZIF-8 @GO		20	203	6.15	-	33.0	-	25	1.97	[55]

20	PSF ZIF-8/GO		5	1.7	0.34	-	5.00	-	25	2.46	[56]
21	PI UiO-66-NH2@GO		5	7.28	0.14	-	52.0	-	25	2.96	[57]
22	PVDF CuBTC/GO		9.5/5	3.3	-	0.049	-	66.3	25	4.94	[58]
23	PSf/DMS		0 10 20	8.55 12.81 28.51	0.3 0.45 1.20	0.34 0.54 1.47	28.5 25.5 23.8	25.1 23.7 19.4	33	4	[59]
24	6FDA-DAM:DABA (3:2)/DMS		0 10 20	134.01 202.09 364.96	5.75 9.12 17.35	3.50 5.58 11.07	23.3 22.2 20.8	38.3 36.2 33.00	33	4	59
25	PSf/MCM-48		0 10 20	4.46 8.45 18.21	0.18 0.32 0.77	0.17 0.33 0.77	24.8 26.4 23.6	26.2 25.6 23.6	33	4	59

26	PSf/MCM-41		0 10 20 30	7.53 10.5 11.4 20.5	0.26 0.35 0.40 0.75	0.39 0.59 0.6 1.07	29.3 29.7 28.9 27.2	19.3 29.7 28.9 27.2	33	4	59
27	PIM-1 Mg(MOF-74)		10 15 20	9.4 45.06 21.26	0.44 1.53 0.74	0.65 2.58 1.11	21.2 29.5 28.7	14.3 17.4 19.1	25	1.97	[60]
28	6FDA-durene Mg2(dobdc)		50	157		-	28	-	35	0.987	[61]
29	PDMS Mg2(dobdc)		10	2.1		-	12	-	25	1.97	61
30	XLPEO Mg2(dobdc)		10	250		-	25	-	25	1.97	61

31	PEBAX (Fumed silica)			60.15			91.14		24,85	7,89	[62]
32	Zeolite			155.8			12.9		24,85	4,93	[63]
33	MoS_2			64					24,85	1,97	[64]

34	PEBAX (ZIF-8)			99.7					29,85	0,98	[65]
35	PEBAX- MIL-53+Benzoic acid			129.1			94.6		34,85	0,98	[66]
36	PEB (ZIF-300)		30% 0	82 54			80 52		24,85	3,94	[67]

37	ZIF-7			41			105		24,85	1,97	[68]
38	MWCNTs			87			53		24,85	1,97	[69]

IV.3 Discussion and interpretation

IV.3.1 Performance of polymer matrix in CO_2/ N_2 gas separation

The data found during our study leads us to plot the variation of the CO_2 / N_2 selectivity as a function of the CO_2 permeability. Based on the results obtained, we observe different trends for permeability and selectivity when adding fillers to different matrix. For some matrix like PSF membranes mixed matrix studied with MCM-41 filler there is increase in selectivity; whereas, we observe a net increase in both permeability and selectivity of PEB with ZIF-300 as filler.

We note that all the mixed matrix membrane family collected in this work dealing to gas separation of CO_2 / N_2 is below the upper limit of Robson, except the case of PEBAX with MOF (MIL-53) as filler. When the points do not exceed or at least correspond to the upper limit of Robson we can say that the performance of the mixed matrix membrane is substandard as showed in Fig IV-1.

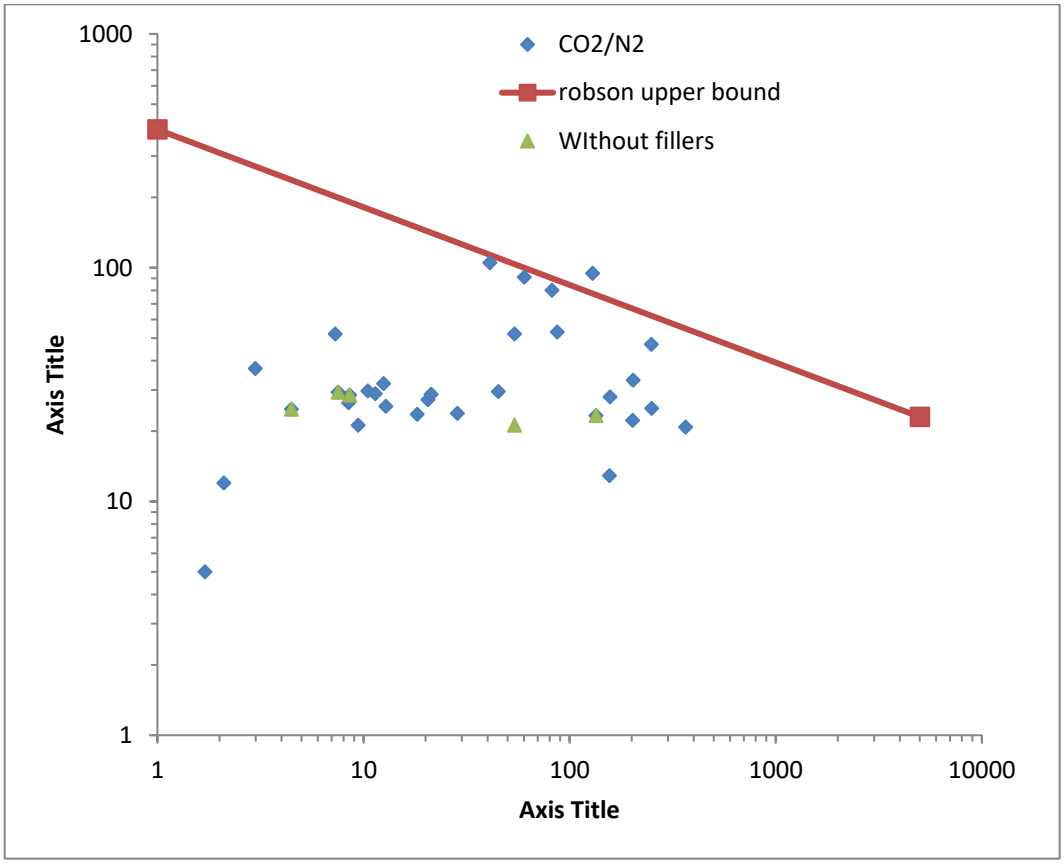


Fig IV-1 Permeaselectivity CO_2/N_2

From the data shown in Figure IV-2 we can say that the higher the permeability of carbon dioxide, the lower the selectivity.

- The figure represents the performance of four types of polymeric membranes for CO/N2 with and without fillers
- Without fillers, the CO_2 permeability and selectivity for each of PSF/DMC membrane, PSF/MCM-48 membrane, PSF/MCM-41 are similar , as the CO_2 permeability was ranging from1 to 10 barrer that selectivity varies between 10 and 50 ,While the co2 permeability of 6FDADAM:DABA(3:2)/CMS tend from 10 to 100 CO_2/N_2 selectivity tend from1to10.
- When fillers were added, permselectivity of major mixed matrix membranes was improved in carbon dioxide permeability, with a slight dip in CO_2 / N_2 selectivity.
- Fr the case of PSF/DMC membrane, PSF/MCM-48 membrane, PSF/MCM-41 was ranging from 10to 100 barrer, the CO_2 permeability of 6FDADAM:DABA(3:2)/CMS was ranging from 100to1000 barrer.

- Among the performance of the above four membranes, we can say that the best performance was that of the FDADAM:DABA(3:2)/CMS membrane in either case with fillers and without. illustrated in Figure IV-2.

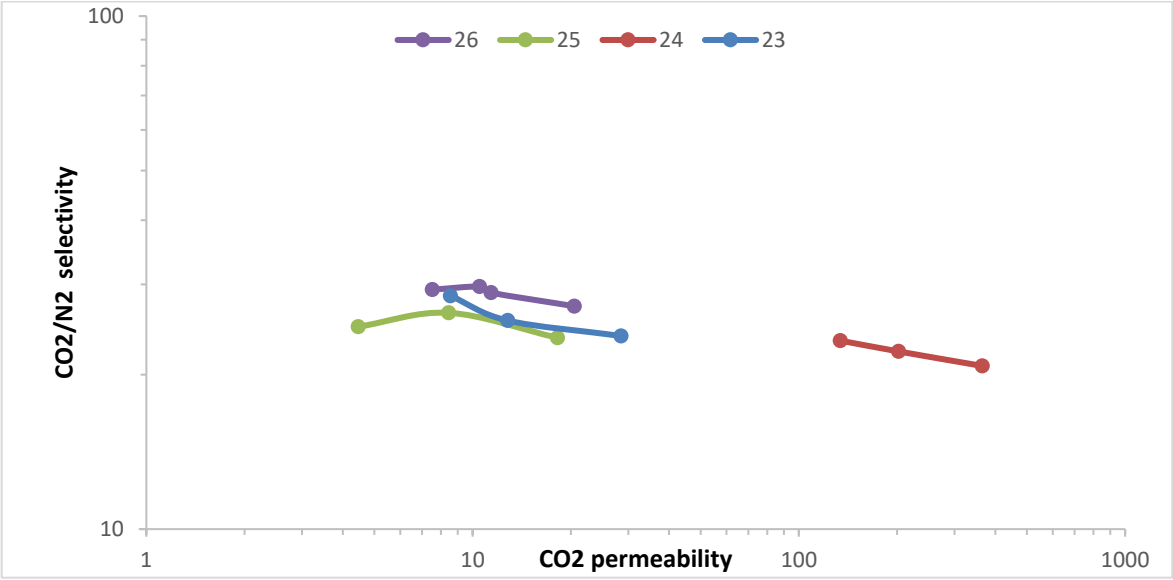


Figure IV-2 variation of the CO_2/N_2 selectivity as a function of the CO_2 permeability for 4 MMMs

IV.3.2 Performance of polymer matrix in CO_2/CH_4

Based on the obtained results, we can state that :

- the whole mixed matrix membranes studied are less effective in meeting the requirement for the current advanced membrane technology as these materials have demonstrated a trade-off between the permeability and selectivity, with an 'upper-bound' evident as proposed by Robeson. As illustrated Fig IV-3.
- We observed different trends for permeability and selectivity when adding fillers to different matrix.
- We noted that membranes without fillers usually have a high selectivity with a low permeability compared to their MMMs

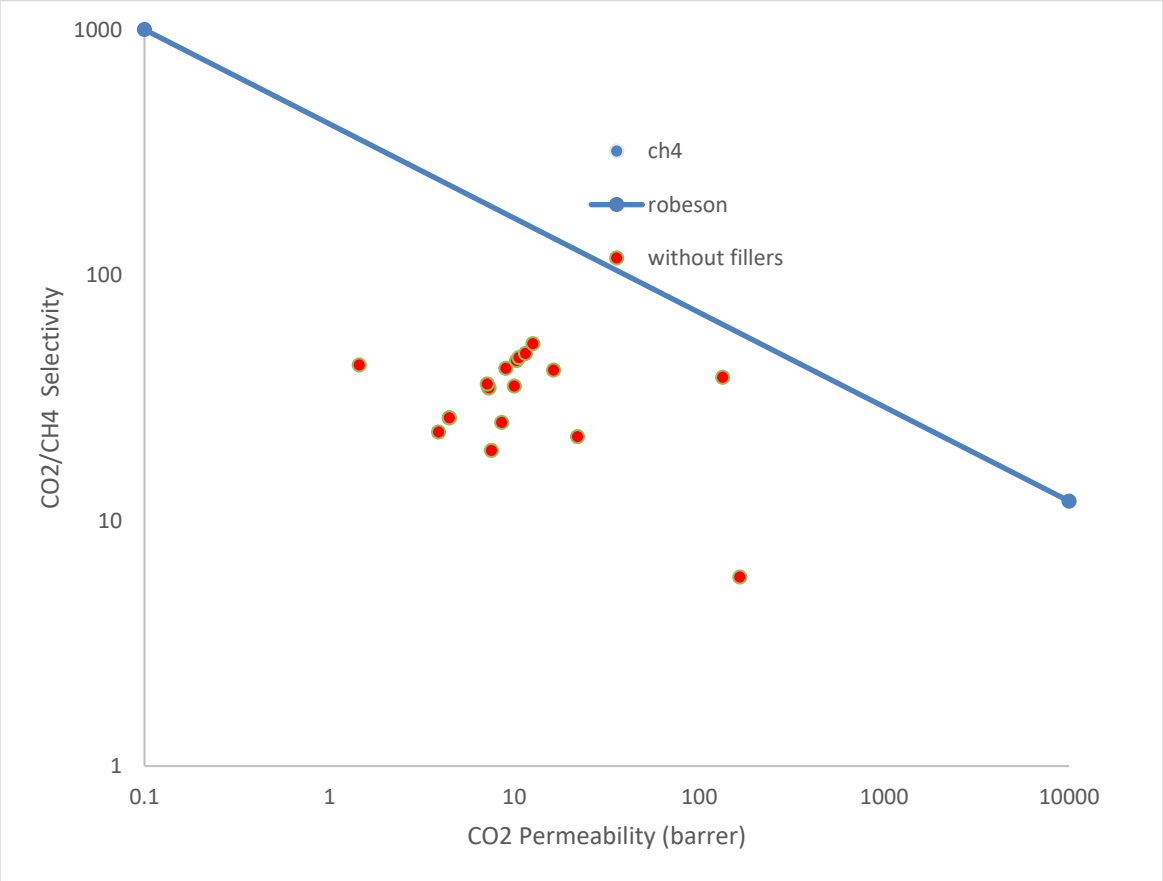


Fig IV-3 Mixed matrix permselectivity performances for the CO_2/CH_4 system

Based on the obtained results we can state :

- The PDMS-41/CNT MMM showed a high CO_2 permeability was ranging from 100 to1000 a low selectivity CO_2/CH_4 varies between 1 and 10.

- The selectivity CO2/CH4 of the both 6FDA-MDA/OAPS and Matrimid®/MOF-5 is high varies between 10and 100 in comparison with the others mixed matrix membrane.
- The PSF/SWNT and PSF/MCM-48 have a similar execution ,they showed a modest permeability was ranging from 1to 50barrer in comparison with PDMS-41/CNT and a approach selectivity to 6FDA-MDA/OAPS and Matrimid®/MOF-51 was ranging from 1to50.
- The PSF/SWNT and PSF/MCM-48 have a similar execution, they showed a modest was ranging from 10 to 50 barrer permeability in comparison with PDMS-41/CNT and a approach selectivity to 6FDA-MDA/OAPS and Matrimid®/MOF-5.
- When we added the fillers we note a big improved in the performance the PSF/MCM-48: the CO_2 permeability.

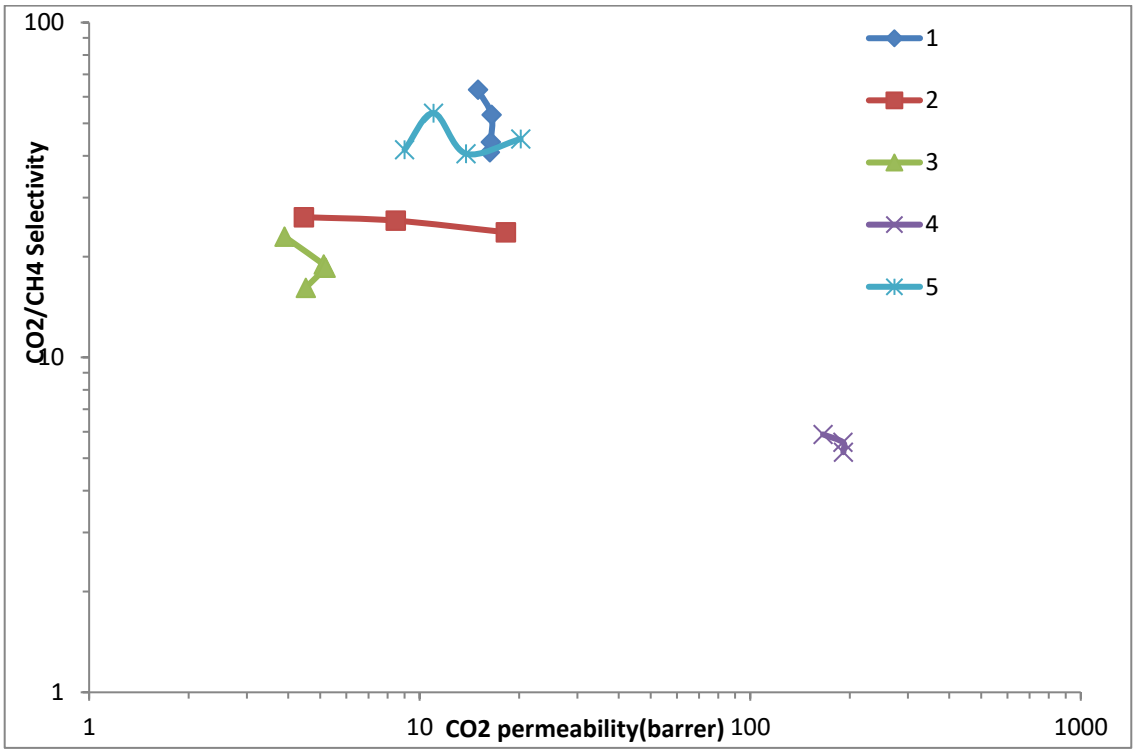


Figure IV-4 Variation of the CO_2/CH_4 selectivity as a function of the CO_2 permeability

IV.4 Filler effect

The adding of fillers imparts more effectively increase co2 permeability, but when the permeability increases the selectivity was decreased as shown in **Error! Reference source not found.**.

- When the membranes had a charge 20% wt of fillers achieved it leads to highest value of CO_2 permeability.
- The membranes without fillers had low CO_2 permeability and a highest selectivity.
- The membranes charge wt10% achieved a modest performance in gas separation.

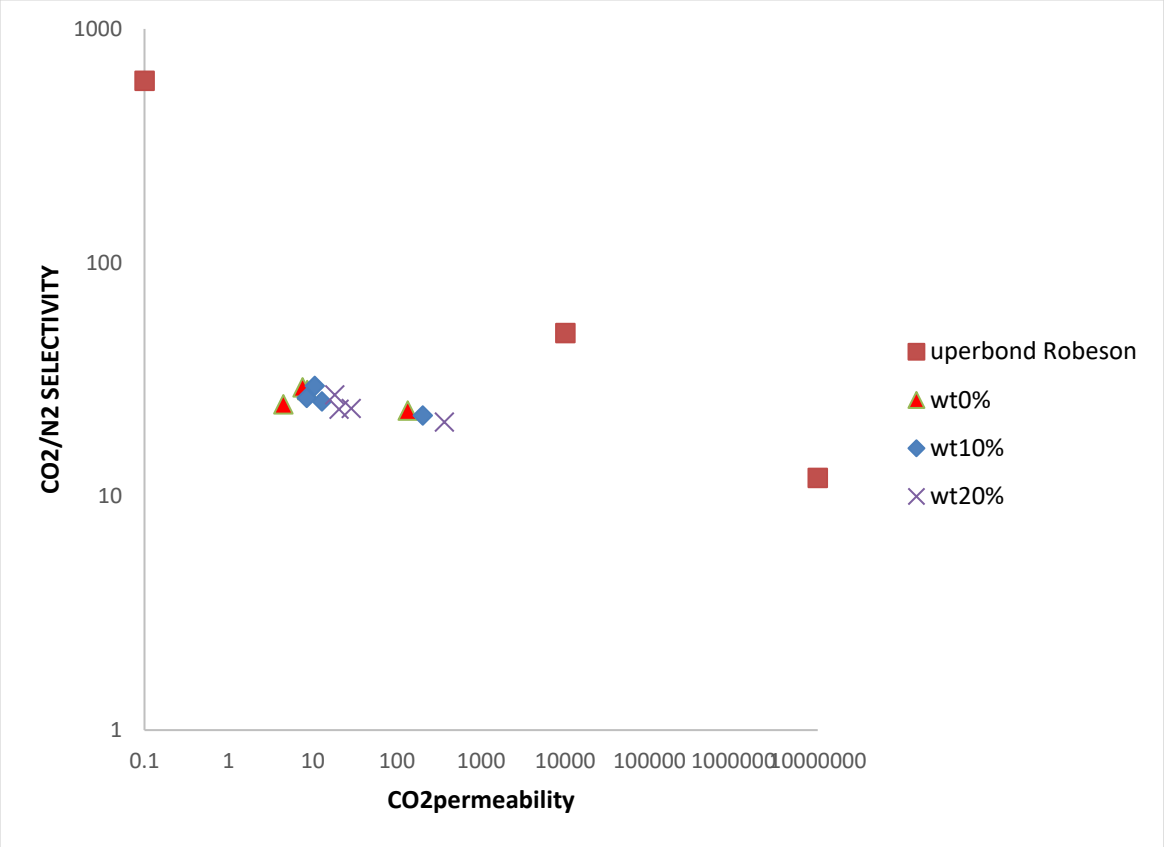


Figure IV-5 permselecticity of the system CO_2/N_2

The remarkable effect of filler is showed in the case of MOF type like in the n° 37 where permselectivity was greatly enhanced. Both permeability and selectivity were increased simultaneously that transcended the 2008 Robeson upper bound for state-of-the-art membranes. the potential of ZIF-300 fordeveloping high-performance mixed-matrix membrane that could be promising for application of CO2 capture.

- Nanoporous membranes are fundamentally different than polymer-based membranes. Their chemistry is different, hence, they do not follow the Robeson limit for a variety of reasons. The simplified figure of a nanoporous membrane shows a small portion of an example membrane structure with cavities and windows. The white portion represents the area where the molecule can move and the blue shaded areas represent the walls of the structure. In the engineering of these membranes, the size of the cavity

(L_{cy} x L_{cz}) and window region (L_{wy} x L_{wz}) can be modified so that the desired permeation is achieved. It has been shown that the permeability of a membrane is the production of adsorption and diffusion. In low loading conditions, the adsorption can be computed by the Henry coefficient.

If the assumption is made that the energy of a particle does not change when moving through this structure, only the entropy of the molecule changes based on the size of the openings. If we first consider changes the cavity geometry, the larger the cavity, the larger the entropy of the absorbed molecules which thus makes the Henry coefficient larger. For diffusion, an increase in entropy will lead to a decrease in free energy which in turn leads to a decrease in the diffusion coefficient. Conversely, changing the window geometry will primarily effect the diffusion of the molecules and not the Henry coefficient.

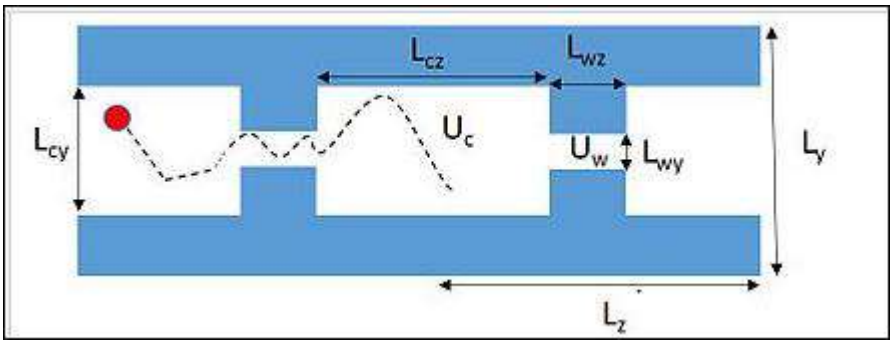


Figure IV-6 Microscopic model of a nanoporous membrane. The white open area represents the area the molecule can pass through and the dark blue areas represent the membrane walls. The membrane channels consist of cavities and windows. The energy of the molecules in the cavity is U_c and the energy of a particle in the window is U_w.

In summary, by using the above simplified analysis, it is possible to understand why the upper limit of the Robeson line does not hold for nanostructures. In the analysis, both the diffusion and Henry coefficients can be modified without affecting the permeability of the material which thus can exceed the upper limit for polymer membranes.[70]

V. Conclusion

At present, few existing membrane materials are inadequate at fully exploiting new opportunities in the gas separation application. The hybrid system in MMM have the potential to address these requirements by synergistically combining the processing versatility of polymers with the separation characteristics of inorganic molecular sieves and has been the subject of numerous researches.

In this work, by screening of the literature, we have collected permeability data of 38 MMMs and study their pearmselectivity performances for CO_2 /N_2 system and CO_2/CH_4. In order to examinate these data we have used Robeson upper band and compared between performances of polymers and their MMMs at different load of fillers.

We stated that MMMs for gas separation contain, as filler : zeolite, CMS, silica particles, CNT, MOFs and ZIFs embedded in different conventional polymer matrix with the ultimate goal of enhancing their permselctivity. The introduction of filler changes chemical affinities of penetrants in nanocomposite membranes which leads in many cases to an increase of permeability with a slight decrease in selectivity. This enhancement is proposed to originate from the strong interactions between the fillers and the polymer matrix

We have noticed a different trend in permselectivity when adding fillers to conventionnel polymers. In some cases, there are no effect. In others many cases, there are a great increasing in permeability only. In third case there a great increase in both selectivity and permeability.

This study has also showed us that, among all fillers, MOFs filler give high permeability and selectivity simultaneously.

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