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# Free volume and mass transport in polymer nanocomposites

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This review relates the free volume properties and the morphology to the mass transport coefficients of polymer nanocomposites. Direct, utilising the method of Positron Annihilation Life-time Spectroscopy (PALS), or indirect measurements of the free volume in the nanocomposites are discussed and the influence of spherical or anisometric nanoparticles on its properties is examined.

## 1. Introduction: polymer nanocomposites

Polymer nanocomposites materials are hybrid systems that consist of a polymeric matrix and dispersed inorganic particles of nanometer scale. When the dispersed inorganic phase consists of spherical nanoparticles with diameter of the order of 50 nm or less, e.g. fumed silica (FS), carbon black (CB), $TiO_2$, the materials are referred to as Polymer Nanocomposites (PN). If the dispersed particles originate from the family of phyllosilicates and have flat shape with high surface area, the composites are called Polymer Clay Nanocomposites (PCN). Some common particles used for PCNs are montmorillonite (MMT), rectorite, hectorite, vermiculite etc.

The creation of a PN or PCN is not a simple issue. In powder form the inorganic phase consists of aggregates or stacks of nanoparticles held together by electrostatic forces. The formation of the nanocomposite requires the deagglomeration of the primary nano-particles or nanolayers (Fig. 1). This can be done if the electrostatic forces between the particles are weakened and the interactions with the organic polymer are enhanced. To exfoliate the clay, therefore, modification of the surfaces of the mineral particulates is needed. The objectives of the modification process are (i) the reduction of the electrostatic forces (swelling) and (ii) the compatibilisation of the filler with the matrix. The latter determines the degree of interaction between the two phases, which is crucial for the final nanocomposite morphology.

The nanocomposites can have excellent mechanical properties. The nano-dimensions maximise the number of available reinforcing elements that carry the applied load in the polymer, while the particles also deflect the evolving cracks. The stress transfer to the reinforcement phase results in significant tensile and toughening improvement. Another major advantage of the nanocomposites is their diverse barrier properties. Spherical nanoparticles can enhance the permeation of gases through the PN, the rate depending on the size of the gas molecule. These materials are good candidates for gas separation applications. On the other hand, PCNs reduce the gas permeation rate because the impermeable clay layers, with their large surface area, force a tortuous pathway for a permeant. These materials are ideal as barrier layers in packaging against the penetration of unwanted gases, e.g. $O_2$, or to prevent gasses like $CO_2$ or $H_2$ to escape. Recent reviews of the methods used for synthesis of PN and PCN and for their various properties can be found in the literature [1, e.g.].

## 2. Free volume

The term “free volume” (f.v.) in a polymer refers to the volume of the total mass that is not actually occupied by the molecules themselves. This is the room that the parts of the chains have to move around. The concept of the free volume is not uniquely defined. Various definitions are often used, such as hole, configurational, fluctuation and excess free volume:

*Hole free volume*: even if the polymer chains were perfectly aligned, there is free space (holes) between them.

*Configurational free volume*: additional free space is created, due to the insufficient chain packing.

*Fluctuation (dynamic) free volume*: the polymer main- or side-chains are not fixed but can move (rotate, vibrate etc.) randomly,

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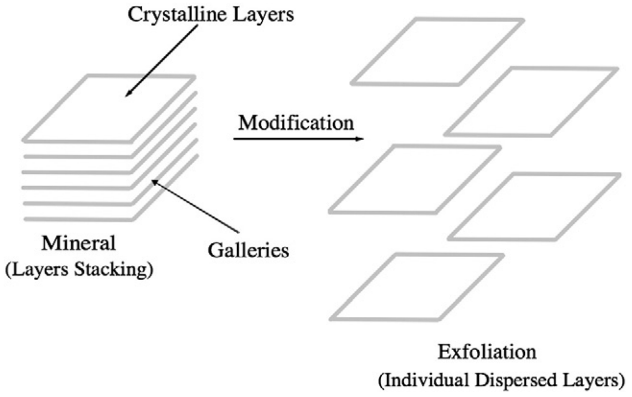

**Fig. 1.** Delamination of the primary mineral particles into individual nano-layers. The layers are located on top of each other like the pages of a book. The Van der Waals gaps between the layers, are called galleries.

due to thermal activation. These motions generate transient gaps, which create extra free volume.

*Excess free volume*: at temperatures below $T_g$, the polymer usually has an actual volume greater than what it would have had, if it had been allowed to cool under equilibrium conditions. The difference between equilibrium free volume and the actual volume under quenched conditions is the "excess free volume" (Fig. 2).

In time, the polymer molecules will try to rearrange themselves, to approach the equilibrium volume of the material, thus eliminating the excess free volume. This time dependent slow decrease in volume is known as "physical ageing" and affects all material properties which change drastically around $T_g$.

The sum of hole and configurational f.v. is the "static" free volume. The excess f.v. may be static or dynamic, depending on the time scale of the relaxation processes. The ratio of static to dynamic excess f.v. is thought to be greater than 1 and depends on temperature.

The static f.v., $V_f = V - V_0$, with $V$ the specific volume of the polymer and $V_0$ the volume occupied by the atoms of the polymer chains at 0 K, is often expressed in terms of the Van der Waals volume, $V_w$, calculated using the group contribution method [2] as $V_0 = 1.3V_w$. The coefficient 1.3 is arbitrary and may sometimes result in faulty interpretations. The fractional free volume is: $FFV = V_f/V$.

The size, shape and position of the polymer f.v. holes vary with time. Around the glass transition temperature, $T_g$, the polymer undergoes a dramatic transformation, as the degrees of freedom of the molecular chains and the resulting mobility change considerably and abruptly.

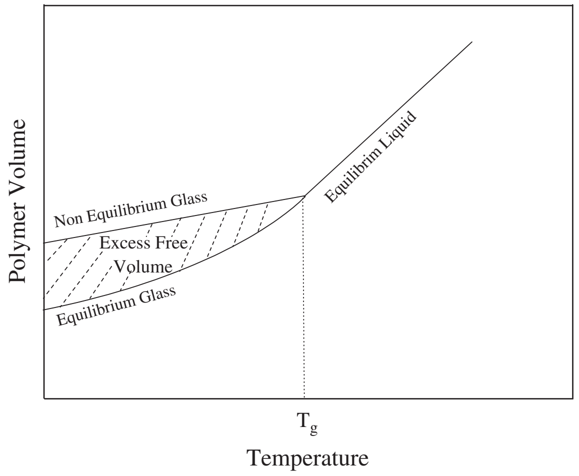

**Fig. 2.** Definition of the excess free volume.

High $T_g$ polymers consist of inflexible chains and are limited in their chain mobility. Low $T_g$ polymers have, in general, more flexible chains and present higher segmental mobility. The higher the chain stiffness, the higher the $T_g$ and the broader the distribution of f.v. hole sizes, since the available variety of chain conformations is restricted.

At $T<T_g$ the segmental motion is frozen and thermal expansion of free volume is almost impossible. In this case, the size, shape and position of the f.v. holes remain constant (very long relaxation times) and a definite, time-averaged Gaussian size distribution of holes, $F(V_h)$, is established. Assuming $N$ spherical holes:

$$F(V_h) = \frac{N}{\sigma\sqrt{2\pi}} exp\left[-\frac{(V_h - V_0)^2}{2\sigma^2}\right]. \tag{2.1}$$

The width of this distribution is:

$$\sigma = \sqrt{\frac{V_h R T_g}{B}}, \tag{2.2}$$

with $B$ the bulk modulus at $T_g$ and $V_h$ the average hole size [3*].

Amorphous polymers in the rubbery state have high chain mobility and short relaxation times. Motions of much longer segments of the backbone chain can take place. These motions are directly related to the increase in free volume caused by the thermal expansion of the system.

$$FFV = (FFV)_{T_g} + \left(T - T_g\right)\alpha_T \tag{2.3}$$

with $\alpha_T$ the thermal expansion coefficient for free volume. The WLF theory gives $(FFV)_{T_g} = 0.025$, $\alpha_T = 4.8 \times 10^{-4}\ \mathrm{K}^{-1}$. The positions of the free volume holes change with time following the motions of the polymer chains. That is, the holes move freely inside the polymer, as no energy change is required for their redistribution.

At a given temperature the number of the holes remains constant, while their size, shape and position vary with time. The number of holes increases with temperature, i.e. additional free volume sites are created. The increase is induced by thermal activation (Brownian segmental motion) and not by an orientational effect. The size of the free volume holes is sensitive to the applied stresses during mechanical deformation but the number of the holes is not affected [4].

Crosslinking does not contribute to changing the free volume size in the glassy state, since the macromolecular motions are frozen (vitrified). In the rubbery state, crosslinking can decrease the free volume, as it confines the mobility of chain segments. The effect is stronger when starting with a looser, mobile polymer network (e.g. crosslinking flexible linear chains). In rigid network structures (e.g. thermosetting polymers) the influence of crosslinking is expected to be smaller.

## 3. Mass transfer coefficients

Gas transport through a polymer membrane is a complex process that includes the sorption of gas molecules on the surface of the membrane; the diffusion through it; and, finally, the desorption of gas from the other surface of the membrane. The permeability coefficient, $P$ (mol $\mathrm{Pa}^{-1} m^{-1} s^{-1}$), of the gas molecules through the membrane is the product of the diffusion coefficient, $D$ ($\mathrm{m}^2 s^{-1}$), and the sorption coefficient or solubility, $S$ (mol $\mathrm{m}^3 Pa^{-1}$):

$$P = D \cdot S. \tag{3.1}$$

These three transport coefficients are discussed separately and their connection with the polymer free volume is analysed in the following paragraphs.