

WATER SORPTION AND TRANSPORT IN POLYMERS

S. Cotugno¹, G. Mensitieri¹, P. Musto² and L. Nicolais¹.

¹ Dept. of Materials and Production Engineering, University of Naples Federico II, P.le Tecchio 80, 80125, Naples Italy.

² Institute of Research and Technology of Plastic Materials, National Research Council of Italy, Via Toiano 6, 80072, Arco Felice (Naples), Italy.

Corresponding author: S. Cotugno.

ph. +39/081/7682410

fax +39/081/7682404

e-mail: scotugno@unina.it

INTRODUCTION

The phenomenology of transport of low molecular weight compounds in polymeric materials has raised in the past 40 years a great scientific and technological interest. There are several engineering applications where diffusion behaviour has a major impact: among many others, gas mixtures separation with membranes, drug delivery, barrier structures for food packaging, environmental resistance of polymer based composites and devolatilization. In this respect, an issue of considerable technological relevance is the durability of high performance matrices for composites. In fact these matrices, when exposed to humid environment, absorb significant amounts of water which adversely affect most physico-mechanical properties.

The main documented effects of water on polymer matrices are, among others, *plasticization*, which occurs by different mechanisms depending on the level of interaction of sorbed water molecules with the matrix; *changes of physical properties*, i.e. decrease of mechanical moduli, decrease of yield strength, change of yield/deformation mechanisms; *hygrothermal degradation*, i.e. microcracks, ageing, chain scission through hydrolysis, degradation of fibre/matrix interface in composites; *swelling stresses*.

In general the plastics and their corresponding composites are sensitive to changes in their environment and their mechanical properties may vary widely with conditions. Therefore, to predict service behavior, it is necessary to have a spectrum of informations showing how a property changes with environmental variables. The environmental degradation of the mechanical properties of the polymer matrix has been generally associated with the plasticization and micromechanical damage induced by the synergistic effects of temperature, stress and sorbed solvents. In this respect a very important role has been played by the plasticization that is the process of depression of the glass transition temperature and reduction of the mechanical properties associated with the sorption of moisture or, more generally, of a low molecular weight penetrant.

Penetrant induced plasticization

Water molecules can be sorbed in different ways in the polymer matrices. For the case of rubbery polymers, water can be molecularly dispersed in the matrix (random dispersion in the bulk of the matrix) or can be interact with specific sites of the macromolecular backbone, when present. Both sorption mechanisms induce a reduction of the T_g of the matrix and the depression of mechanical properties. In the first case (simple dilution mechanism) the T_g depression is related simply to an increase of the volume, while in the case of specific interactions, the sorption process can be related to the distribution of intermolecular physical bonds (e.g. hydrogen bonds) which induce a decrease of T_g and of mechanical properties. In the case of glassy polymer matrices, due to non equilibrium state of the material, an additive sorption mechanism is active associated to the adsorption on microvoids present in the matrix. This adsorption mechanism is not likely to precedent T_g depression. However, also in this case, plasticization is essentially associated to the same mechanisms mentioned for rubbery polymers.

These phenomena are evident in the figure 1, the sorption of gas and vapors in the glassy systems can be modeled by superimposing Henry's and Langmuir type isotherms.

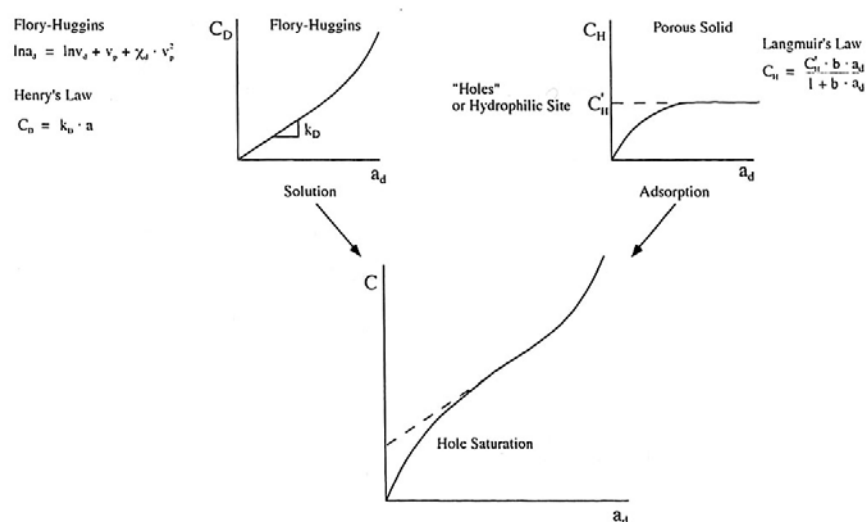
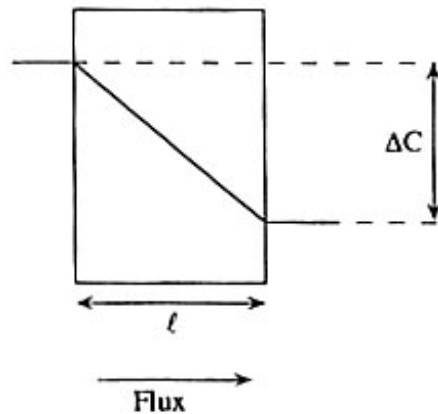


Figure 1.

As reported in figure 2 the generally accepted mechanism for penetrant sorption in the polymers is an activated sorption-diffusion process. The molecules are first dissolved into the polymer surface and then diffuse throughout the bulk of the polymer by a series of activated steps. The mass transport of low molecular weight compounds in the polymer has different features if the matrix is in the glassy state ($T < T_g$) or in the rubber state ($T > T_g$). As mentioned, while the specific volume of a liquid-like amorphous polymer above the glass transition is always at its equilibrium value, the glass formation induced, as a consequence of reduction of polymer segmental mobility, an out of equilibrium excess free volume. The effect of water absorption on the mechanical properties of the matrix can be analyzed through mechanical tests performed on samples of the neat polymer subjected to different aging conditions. As an example, the measured tensile yield strength (T.Y.S.) in the case of Nylon-6 exposed to different water environments is reported in the table 1. The expected plasticization effect is evident by a 50% reduction of T.Y.S. Once dried again, the sample

Solution - Diffusion



$$J = -D \frac{\Delta C}{\ell}$$

J = Mass flux

D = Diffusion coefficient

$\frac{\Delta C}{\ell}$ = Concentration gradient

Sorption Equilibria

Solvent-Polymer Solution depends on:

- a) Temperature
- b) Polymer-Penetrant affinity
- c) Polymer state (glassy or rubber)

Diffusion

Penetrant Transport is:

- a) Temperature activated process
- b) Penetrant size and shape dependent
- c) Polymer morphology dependent (crystallinity, segmental mobility, presence of interacting group)

Figure 2.

does not attain in the original T.Y.S. suggesting that exposure to water environments induce permanent changes in the matrix.

Table 1

Condition	Tensile Yield Strength (MPa)
Dry	57.4
Water immersion (2 days at 25°C)	29.7
Water immersion (20 days at 25°C)	27.7
Desiccated	50.3

Figure 3 shows the water uptake curves in the case of nylon 6.6 and its composites ($V_f=0.19$, volume fraction of glass fiber) conditioned at 25°C, 60 and 100°C. In all cases M_t (water mass uptake into the polymer matrix) increases with $t^{1/2}$ (where t is sorption time) and then slows down until an equilibrium water content, M_m is reached.

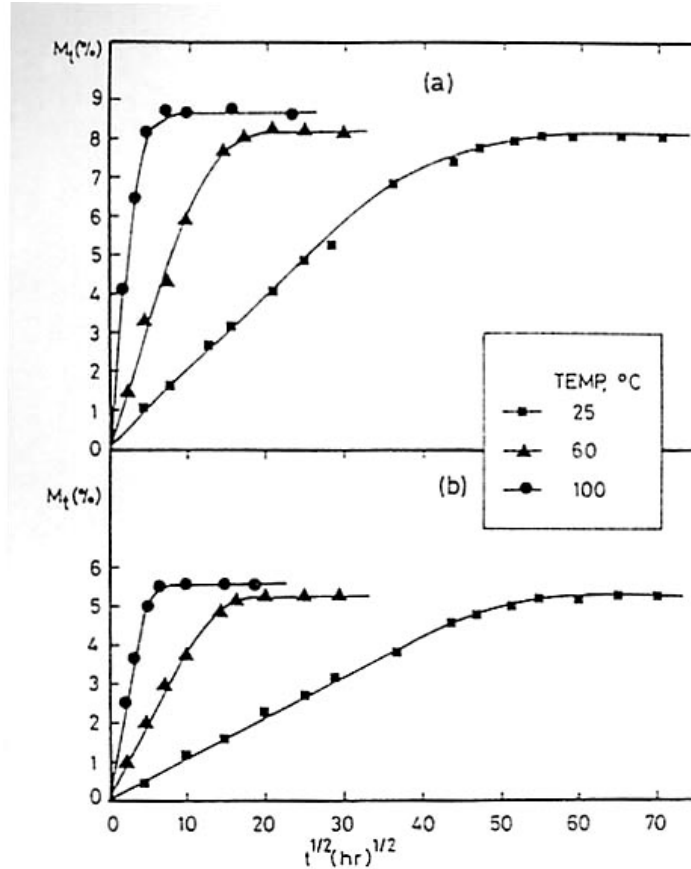


Figure 3

A good agreement is obtained between experimental data and theoretical prediction based on Fickian behavior [Crank J., *The Mathematics of Diffusion*, 1975] (see eq. 1):

$$\frac{M_t}{M_m} = 1 - \frac{8}{\pi} \exp\left[-\left(\frac{Dt}{l^2}\right)\pi^2\right] \quad (1)$$

where : D = diffusion coefficient

t = time

l = thickness of sample

As shown in the figure 3, while the equilibrium content is almost independent of temperature, the diffusion rate which is given by the slope of the curve is greatly influenced by temperature. The time required to attain equilibrium water content is reduced as the immersion temperature increase. The diffusivity, D , can be calculated from the initial linear portion of the absorption curve as:

$$\frac{M_t}{M_m} = \left(\frac{4}{l}\right)\left(\frac{D}{\pi}\right)^{1/2} t^{1/2} \quad (2)$$

On the basis of the previous arguments, its evident that matrices display hydrophilic sites are much more sensitive to moisture as compared to hydrophobic polymers. In the following a comparison between an hydrophobic polymer (ethylene-

propylene-CO terpolymer) and commercial nylon-6 is briefly presented [Mensitieri G., *Polymer*, **1995**]. The analysis is limited to water sorption at 35°C. Water sorption isotherms were determined for a “cast” and bioriented nylon-6 at 35°C, the results are compared to terpolymer in the figure 4.

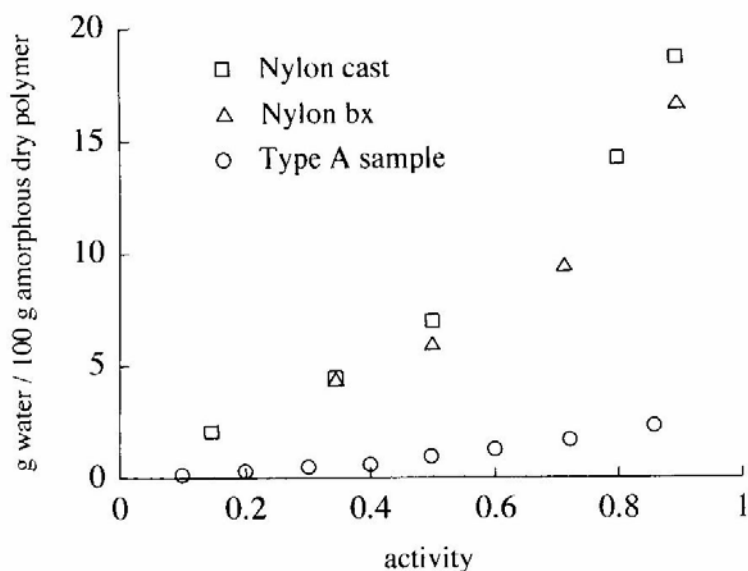


Figure 4

As expected, the amount of sorbed water is much higher in the case of nylon-6 due to high interaction of water with polymer matrix. The breakage of hydrogen bonds, brought about by sorbed water in nylon-6 causes a considerable plasticization of the system. An under estimated T_g depression for both types of nylon-6 at different levels of sorbed water concentration as theoretically predicted by means of the equations proposed by Moy and Karasz [Moy P., Karasz F.E., *ACS Symp.*, **1980**] are reported in the table 2. Actual values of T_g are even lower due to H-bonds breaking. The hydrophobic terpolymer displays a much lower T_g depression.

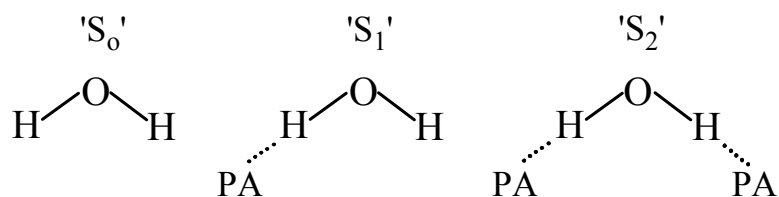
Table 2.

Water activity	Sorbed water (g water/100g amorphous phase)		Calculated T_g (°C)	
	Nylon	Terpolymer	Nylon	Terpolymer
0	0	0	46.5	17
0.347	4.40	0.569	14.3	4.8
0.502	6.00	0.968	6.2	-2.7
0.714	9.50	1.706	-13.4	-14.7
0.897	16.60	2.522	-34.6	-25.7

State of sorbed water molecules in interacting and non interacting matrices

Since the plasticization extent is related to the type of interaction that water molecules establishes with the matrix, its extremely important to investigate the state of water molecules sorbed in the polymers. A very effective technique is the *in-situ* FTIR [Cotugno S. et al., *Polymer*, **2001**] which allows the detection of differently interacting water molecules. An instructive example showing the efficiency of this experimental approach is supplied by the comparison of water sorption in highly interacting (epoxy resin) and low interacting (polyimides) macromolecules systems.

The subtraction spectrum of the two matrices exposed to liquid water in the 3800-2800 cm^{-1} region was interpreted on the basis of a simplified association model, whereby three different water species (S_0 , S_1 and S_2) can be spectroscopically distinguished, according to the reported scheme 1.



Scheme 1,

The figure 5 displays the experimental subtraction spectrum along with its curve-fitting analysis for the case of a film exposed to a water vapour activity equal to 0.8 at 24°C, for epoxy resin; similar profiles are determined at the other investigated activities.

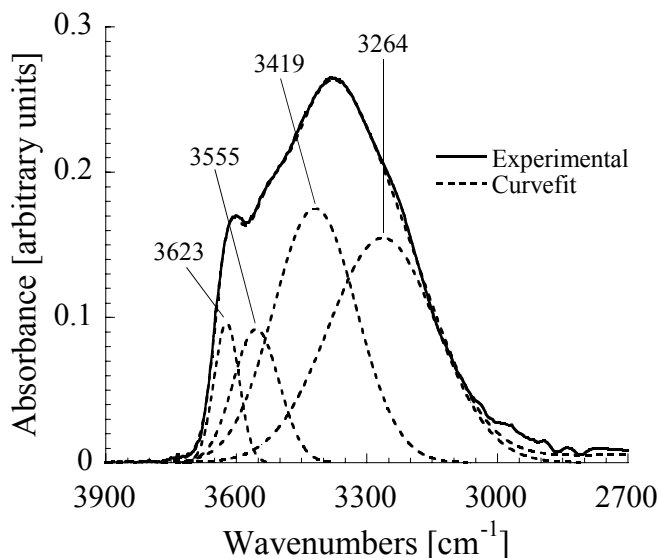


Figure 5.

The peak centred at 3623 cm^{-1} is related to unassociated water (i.e. water which does not establish any H-bond, S_0); the whole broad band at lower frequencies is due to hydrogen-bonded water molecules (S_1 , S_2). Figure 6 displays the experimental subtraction spectrum, along with its curve-fitting analysis, for the case of a non-interacting matrix film exposed to a

water vapour activity equal to 0.4 at 30 °C. The profile is significantly different from the previous one: the high frequency peak, associated with the S_0 species, becomes the dominant component. Other two peaks, related respectively to S_1 and S_2 species, are present, even though their relative contribution is much lower than in the case of the epoxy. In this system, it is likely that the S_1 and S_2 species represent self-associated water molecules, since the polyimide has no strong proton accepting groups along its backbone. In particular, S_1 species are mostly contributed by dimeric water, while the S_2 species are due to water forming clusters of more than two molecules.

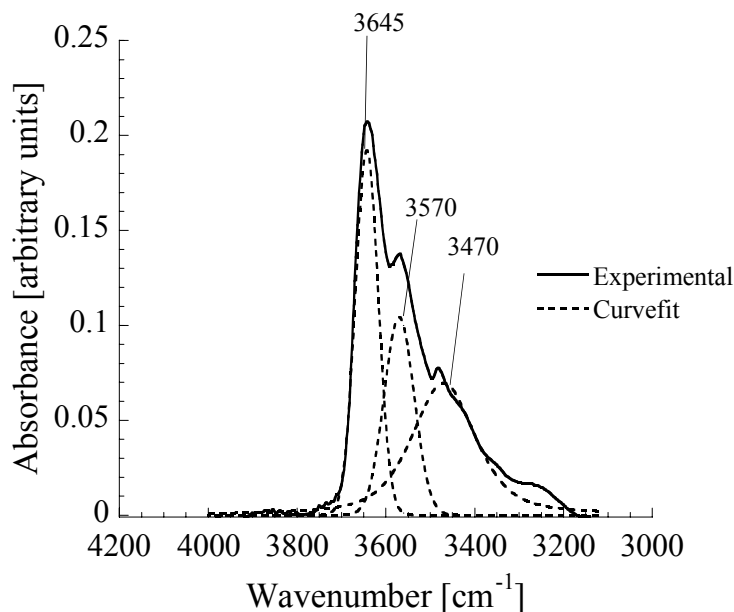


Figure 6.

In the case of the interacting matrix, the water species not interacting with the network

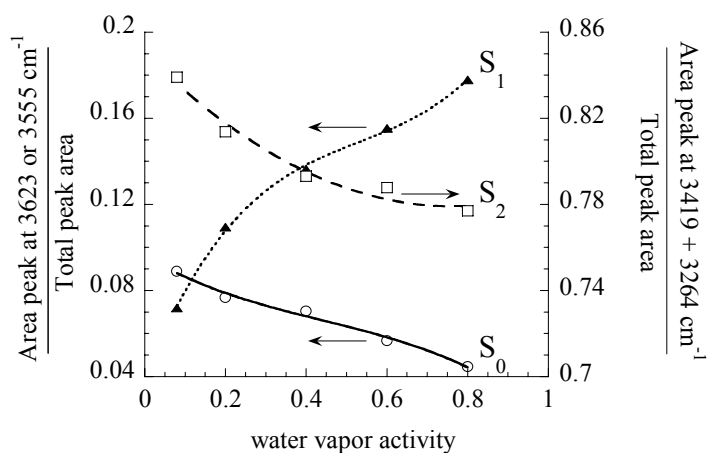


Figure 7.

(S_0 and S_1) are expected to be characterised by high molecular mobility and low plasticizing efficiency. These species should be confined into excess free volume (microvoids) or molecularly dispersed with no H-bonding interactions (bulk dissolution). Conversely, S_2 molecules are firmly bound to specific sites along the polymer network, thus exhibiting a much lower mobility and a higher plasticizing efficiency.

In the case of the non-interacting matrix, there is no evidence of penetrant molecules directly bound to the network. Therefore, all the penetrant molecules are either confined in microvoids or molecularly dispersed with no H-bonding interaction with the substrate. Also in this case, a lower mobility is expected for S_2 species; however the origin of this effect is now related to the increased volume of the clusters or, alternatively, to the increase of activation energy associated to a diffusive jump (detachment of a single water molecule from the cluster).

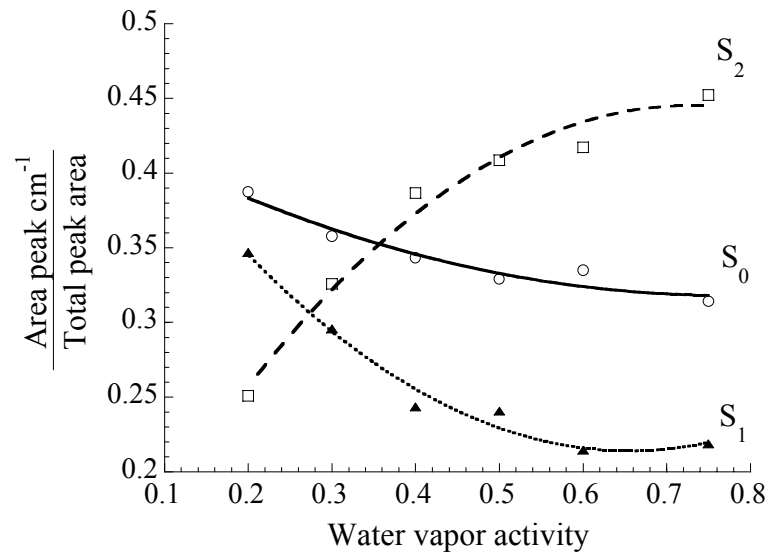


Figure 8.

On the basis of the above considerations, a lower plasticizing efficiency of absorbed water molecules is expected in the case of the polyimide with respect to the epoxy. The relative contribution at sorption equilibrium of the different water species as derived by the curve fitting analysis of the equilibrium subtraction profiles are reported as a function of water vapour activity in figure 7 for the epoxy and 8 for the polyimide.

CONCLUSIONS

In present work are discussed mass transport and diffusivity of water in polymer in the glassy ($T < T_g$) and rubbery state ($T > T_g$), and their effects on mechanical properties (T.Y.S. depression, plasticization, T_g depression, etc.).

The water sorption in polymer induce a decrease of T_g which effect on mechanical properties can be analyzed by measuring of tensile yield strength, that in the case of nylon-6 displayed 50% reduction respect to dry sample. This effects increases with concentration of water in polymer and is dependent by specific interaction between matrix and water

molecular. In this respect, the interactional aspects related to sorption and transport of water molecules in polymer has been deeply investigated by *time-resolved* FTIR spectroscopy. As model systems for interacting and non-interacting matrices a tetrafunctional epoxy resin (TGDDM-DDS) and a polyimide (PMDA-ODA) have been considered. The presence of different species of absorbed water has been evidenced in both materials, characterized by different level of interaction with the matrices and, therefore, plasticization efficiency. In the case of epoxy, free and dimeric water molecules coexist with water molecules strongly bound to the polymer network through H-bonding interactions. Conversely, in the case of polyimide mostly free and self-associated water has been detected. Consistently with the different degree of molecular interaction, the two systems behave differently with respect to their mechanical properties.