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Wettability of Acrylate Copolymer Surfaces after Ageing in Water

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Summary: Contact angle measurements (captive bubble and sessile drop techniques) were used to determine the surface energy of several acrylic based polymers at the early stage of immersion (t_0) in pure and salt water or after several days (t_x). The sessile drop technique using various liquid probes allows the calculation of the dispersive, acid and basic components of the surface energy. Significant differences of wettability are observed between the polymers at t_0 which tend to remain after immersion along with a general increase of the surface hydrophilicity. The same trend is observed by the ''in-situ'' captive bubble technique. The surfaces become more hydrophilic with a final contact angle, θ, ranging from 110 to 150 ± 3° in pure water and 130 to 150± 4° in 0,51 M salt water. The modifications of surface energy between t_0 and t_x are not only dependent on water diffusion. One assumption is that the degree of swelling of the immersed surface layer along with the particular dynamics resulting from a surface gel-like structure are significant factors in the measured surface thermodynamics.

Keywords: captive bubble; contact angles; copolymer; hydrophilic/hydrophobic acrylate polymers; water ageing

Introduction

The evolution of the international, environmental legislation is moving towards a total withdrawal of organotin compounds and to a severe limitation of the use of cuprous oxide and of organic molecules in antifouling paints. To develop new antifouling strategies without added toxic products, it is necessary to further understand the phenomena of bioadhesion in relation with polymers surface characteristics. Erodable paints are blends or copolymers enclosing hydrophilic, hydrophobic and hydrolysable units.[1,2] In contact with water this polymeric systems exhibit a very complex surface structure (hydration, swelling, association between hydrophobic sequences, hydrolysis, appearance of polyelectrolyte sequences, segregated domains) which can be compared to a gel-like structure.[3]

The surface energy of hydrogels for instance has already been investigated[4,5] by sessile drop or captive bubble techniques. It is often suggested that these highly hydrated polymers are

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capable of surface reconstruction through reorientation of polymer chain segments depending on the nature of the adjacent phase. This has also been demonstrated for hydrophobic glassy polymers aged in water at temperatures close to their Tg.[6] The effect of the conditioning medium (pure or salt water, presence of organic molecules) on the polymer surface wettability has been described in the literature.[7] The effect of electrolyte or surfactants adsorption on the contact angle on polymer surfaces is still controversially discussed.

In this paper, four different additives free polymers used in anti-fouling paints formulations were investigated. The evolution of the surface tension with immersion time was studied as well as the effect of adsorption of electrolyte. These results will be discussed in terms of polymers hydration, dynamics in gel-like structure and surface chains reorientation and hydrolysis.

Materials and Techniques

The polymers synthetized by radical polymerisation were so-called, R1, Ter, Pla and 80. R1 is a commercial copolymer of methyl methacrylate (MMA) and butyl methacrylate (BMA). Ter coresponds to a terpolymer based on the association of 2, 4, 5-trichloro phenyl acrylate (TPA), terbutyl acrylate (tBu), dimethyaminoethyl acrylate (DMAM). Pla is a copolymer of lactic acid (LA) and tertbutyl acrylate repeat units. 80 is a copolymer of tertbutyl acrylate and dimethylaminoethyle methacrylate (DMAM).

Table 1. Composition and properties of the polymers.

Name	Composition	Tg (°C)	Microstructure	Mn	Hydration (%)	
					t_0	t_F
R1	MMA/BMA	46	statistic	_	0,25	0,25
Ter2	TPA50/tBu30/DMAM20*	50	short TPA blocs	15k	0,5	10
Pla	Pla/10tBu*	23	grafted LA	75k	0,5	1,5
80	tBu80/DMAM20*	30	patially bloc	15k	1	1

* The number indicated after each monomer is the molar percentage exept for Pla/tBu for which 10 is the number of tBu repeat units for one LA. The trend for the copolymer microstructure is based on the Lewis-Mayo approach at low conversion ratios. t_0 and t_F represents the initial and 15 days hydration percentage drawn from ref.[8] respectively.

The polymers were spin-cast from a 15 % acetone solution on a microscope glass slide. Contact angle measurements (captive bubble and sessile drop technique) were carried out with a Digidrop apparatus (GBX company) to determine the surface energy at the early stage of immersion (t_0) in pure and salt water or after several days (t_x) at room temperature. The sessile drop technique using various liquid probes (tricresyl phosphate, water, formamid) allows the calculation of the dispersive, acid and basic component of the surface energy according to the van Oss theory.[9] The time evolution of the air/water contact angle is followed by the ''in-situ'' captive bubble technique.

Results

As observed in Figure 1, significant differences in the contact angles of the captive bubble are observed between the polymers at t_0. Hence, Ter2 and 80 polymer are found rather hydrophilic whereas R1 and Pla are more hydrophobic. These results are consistent with the chemical nature of the monomers and, therefore, allows us to validate the captive bubble method.

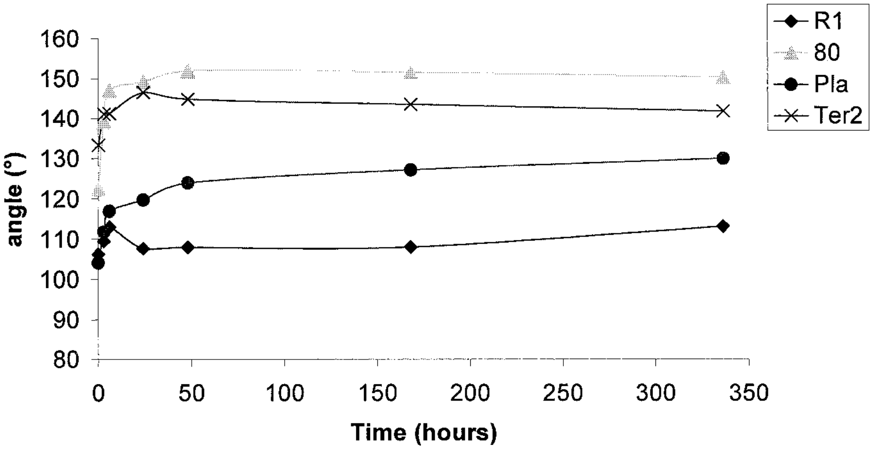

Fig. 1. Evolution with the ageing time of the contact angle of a captive air bubble in pure water.

After 350 hours of immersion, all the polymers except R1 have significantly increased heir hydrophilic character. This trend has been ascribed, for hydrophobic polymers such as polyethylene-vinyl acetate, polyethylene-maleic anhydride or polymethacrylate, to polar side chain reorientation towards the water polar surrounding medium.[6] Nevertheless, it has been observed that these surface conformational rearrangements only occur at temperature above 80°C although the local side-group relaxation (β-relaxation) is allowed well below this range of temperature. It can be concluded that local side-goup reorganisation are not sufficient to allow significant modification in the surface wettability. Larger scale rearrangements are therefore required to significantly modify the surface wettability that are normally hindered well below Tg. This is the case of R1 which captive bubble contact angle does not significantly increase after 15 days of immersion at room temperature.

The driving force for these modifications of wettability of partially hydrophilic polymers such as 80 and Ter2, is much more complicated. Pla can also be considered as a partially hydrophilic polymer since water induced side chain hydrolysis yield to the appearance of hydrophilic groups. The fraction of hydrolysed groups after 350 hours of immersion in water is 0,10 and 0,04 for Pla/tBu and Ter2, receptively. Water diffusion in the film yields an increase of the degree of swelling which, in turn, increases the molecular mobility and, therefore, the ability of the polymer to reorient its surface chemical polar groups. However, two copolymers, 80 and Ter2, which end up after 15 days in water with same contact angle, namely, around 150°, have a totally different percentage of hydration (80: 1%, Ter2: 10%). The influence of the mobility has to be taken into account since the Tg of 80 is close to the room temperature whereas the Tg of Ter2 is 50°C. Indeed, diffusion and relaxation are two mechanisms which are of course correlated but depend on the state of the amorphous phase. Fickian diffusion is often observed for polymers in the rubber state since diffusion is slower than the relaxation whereas in the glassy state non Fickian diffusion is mainly due to local dynamic heterogeneity. The time evolution of the contact angle of the copolymers under study does not follow a simple Fick law. Pla and 80 polymers are in the glassy state at room temperature, but since their Tg is close to 30°C, absorption of a small amount of water will rapidly modify the chain dynamics from glassy to rubber behaviour. A depression of the glass transition induced by water sorption leads to negative Tg value meaning that polymer is in a rubber state at room temperature after several days of immersion.

Advancing and receding angles were obtained from sessile drop measurements by increasing and decreasing the volume of the water drop. The difference between the two angles provides the hysteresis which is known to be related to the surface heterogeneity (chemical or topological). The hysteresis are in average 5, 6, 11 and 20 for R1, Pla, 80 and Ter, respectively. The two last copolymers are those which exhibit a bloc microstructure which might strongly increase the surface heterogeneity and, therefore, the measured hysteresis.

The use of various liquids probes allowed the determination of the acido-basic character of the polymer surface according to the van Oss theory. The Lifshitz-van der Waals component, γ^{lw}, as well as the acidic (electron acceptor) component, γ^{+}, of the surface energy remain quit constant for the four polymers after ageing in water. In contrast, the basic character (electron donator), γ^-,of the polymer surface increases from 3 to 27 mJ/m^2 for R1, from 11 to 13 mJ/m^2 for 80, from 7 to 11 mJ/m^2 for Pla and from 19 to 24 mJ/m^2 for Ter. The largest increase of the surface basic character concerns R1 which starts with the lowest value and ends up with the highest one despite its high Tg value. The slight increase of γ^- for the other polymers is ascribed to the water induced surface rearrangements as described in the previous paragraph. However, no direct correlation can be made between the evolution with time of the captive bubble contact angle and the acido-basic component of the surface energy measured by the sessile drop technique. We assume that fast relaxation of the surface oriented side-groups, as well as rapid surface water evaporation after removal of the sample from water, can strongly minimise the measured surface energy. The high γ^- measured for R1 can therefore be explained by a low relaxation rate since this copolymer has the higher Tg value. Moreover, the surface gel-like structure of the hydrophylic polymer surface in water might be partially lost in air due to the collapse of the water dangling chain segments. Surface chain entropy in contact with air is totally modified as compared with that in water, explaining the observed differences between the two used techniques.

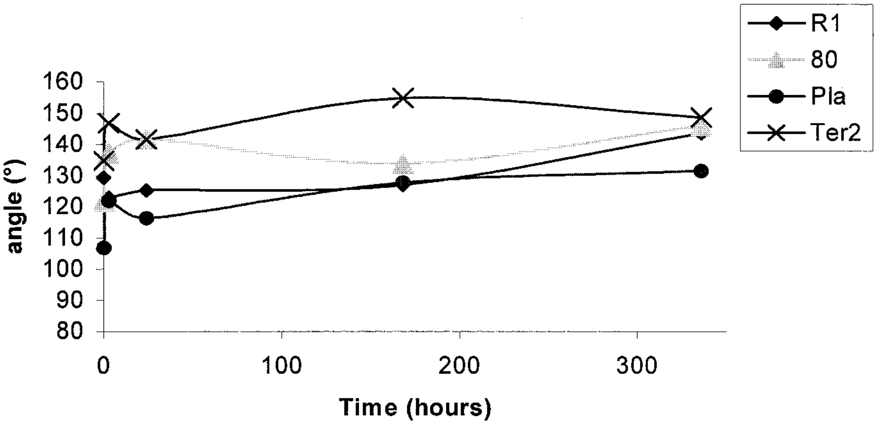

Fig. 2. Evolution with the ageing time of the contact angle of a captive air bubble in 0,51 mol/l NaCl water.

0,51 mol of NaCl was added to the water and the evolutions of the contact angle of the captive bubble are plotted in Figure 2. The wettability of the polymers is strongly affected by the addition of the electrolyte in comparison with pure water. This is essentially true after a few days of immersion since all the polymers tend towards a high hydrophilic character with a contact angle ranging between 130 an 150°. Less attention has been paid to the effect of electrolytes on the contact angles on polymers surfaces. Some researchers have reported that on non polar polymers no influence of the electrolyte or pH has been observed.[6] However, polymers embedding functional polar or ionizable groups can behave very differently according to the ionic strength of the solution. Poly(lactic/glycolic acid), for instance exhibit a strong pH dependence of the contact angle after 8 days of soaking in distilled water. Hydrolysis of the side groups providing a polyelectrolyte character to the polymer is responsible for the particular behaviour of this polymer in a buffer solution.

Ter, Pla and R1 are partially hydrolysable copolymers or blend which can present ionic groups at their surfaces after a few days of immersion. Potential ion-ion or ion-dipole interactions of polymer groups with the Na^+ or Cl^- ions can strongly alter the wettability of the polymer. It has been claimed that since cations have significantly higher hydration energies than anions, a higher anion concentration is expected on a surface[7] The specific adsorption of anions at polymer surfaces can explain the increase of hydrophilic character of initially hydrophobic R1 copolymer, for instance.

Conclusion

The choice of the contact angle measurement technique is a compromise between accuracy (captive bubble) without any available information on the acido-basic character of the polymer or more detailed information (sessile drop) on the surface energetic with moderate accuracy (surface hydration, partial relaxation, surface water structure). An increase of the hydrophilic character of the copolymers after immersion has been highlighted in this study which is ascribed to a particular orientation of the polar side groups towards the polar water medium. The presence of electrolyte in the water increases the hydrophilicity of the initially hydrophobic copolymers presumably due to anion specific adsorption.

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