



A model for diffusion-driven hydrophobic recovery in plasma treated polymers

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ABSTRACT

Plasma treatment is widely used for polymer surface modification and, in particular, for the improvement of its adhesive properties. After such treatment the surface energy increases and therefore adhesion increases. However, the change of surface properties is not permanent. Following the treatment, the surface undergoes a relaxation process, called hydrophobic recovery, after which it restores, at least partially, its original low surface energy. Different mechanisms can be responsible for the observed hydrophobic recovery including the diffusion of polar groups and molecular reorientation. We propose a model for the hydrophobic recovery due to a combination of two thermodynamically non-equilibrium processes: diffusion and molecular reorientation. The model explains the mechanism of the hydrophobic recovery and fits well the available experimental data.

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1. Introduction

Plasma treatment is used to alter wetting and adhesion properties of many polymeric surfaces by changing their surface roughness and chemical structure. This can lead to novel materials, having superhydrophobic [1], oleophobic [2], superhydrophilic [3] or self-healing [4] properties. In particular, plasma treatment is used to increase the surface energy in order to increase adhesion [5]. Low surface energy and chemical inertness of some polymers, for example, polytetrafluoroethylene (PTFE), has limited their application to the cases where high adhesion is desired. Plasma treatment in this case results in the introduction of polar functional groups, such as carboxyl (–COOH) and hydroxyl (–OH) on the surface [6,7].

The water contact angle (CA) is the main parameter which characterises wetting of a solid surface. The CA depends on surface energy and roughness. Typically, plasma treatment makes the surface more hydrophilic, i.e., decreases the water CA. However, longer treatments can increase the CA due to the increase in the surface roughness. An optimum plasma treatment time and plasma power is usually determined corresponding to minimum water CA and maximum adhesion.

This surface modification, however, is not permanent. The plasma treated surface experiences an increase in the water CA and decrease in surface energy over time. This phenomenon is called hydrophobic recovery. Different mechanisms have been proposed to explain the hydrophobic recovery in different polymers.

For polydimethylsiloxane (PDMS), this phenomenon is attributed to the transport of low molecular weight species from the bulk to the thermodynamically unstable hydrophilic surface. Plasma treatment results also in the introduction of nanoscale roughness at the PDMS surface. It has been shown that not only the migration of low molecular weight species, but also the relaxation of the surface roughness is responsible for the observed hydrophobic recovery in PDMS [8].

Different mechanisms can be responsible for the observed hydrophobic recovery: diffusion of non-modified low molecular weight species produced by plasma treatment from the bulk to the top most layers [9], diffusion of oxidised low molecular weight species from the top most layers to the bulk, diffusion of non-modified macromolecules to the surface, reorientation of polar chemical groups into the bulk of the polymer.

The rate and extent of hydrophobic recovery can be influenced by many factors such as storage condition, treatment gas, treatment time, temperature and humidity [10]. The molecular structure and the mobility of the polymer chains are other important factors. Rotational and translational motion of macromolecule chains and chain segments enable the treated surface to rearrange and recover to a state with minimised surface energy [11]. The glass transition temperature of polymers is an important parameter reflecting the mobility of macromolecular chains. A more stable treatment (less recovery) can be obtained with polymers having higher glass transition temperature [12]. The degree of crystallinity in crystalline polymers controls the chain mobility, and as a result can affect the hydrophobic recovery. The higher the degree of crystallinity, the more stable is the plasma treated surface [13]. Cross-linking is another factor that can restrict the chain mobility and reduce the hydrophobic recovery. Morent et al. [14] investigated the influence

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of operating gas during plasma treatment on two different polymers, polyethylene terephthalate (PET) and polypropylene (PP) in air, helium and argon. The lowest recovery (the highest stability) was obtained for the polymers treated in argon due to high cross-linking degree. Ren et al. [15] investigated the plasma treatment and the hydrophobic recovery of ultra high modulus polyethylene (UHMPE) fibres by using helium and helium/oxygen mixtures. Plasma treatment resulted in the formation of polar group, and decrease in water CA's in helium and helium/oxygen mixtures. The treatment was more significant for the 1% oxygen/helium atmosphere compared to the pure helium or 2% oxygen/helium atmospheres. They proposed that a small amount of oxygen facilitates the formation of atomic oxygen which is needed for surface treatment.

From the thermodynamic point of view, hydrophobic recovery is a non-equilibrium process. The material is driven away from the thermodynamic equilibrium by the effect of plasma, which creates concentration gradients of the polar groups. After the treatment, the material slowly returns to the equilibrium state and minimises its surface energy. This process is similar to the healing of cracks in a self-healing material [3]. Below we propose a model for the recovery due to diffusion and molecular reorientation.

2. Hydrophobic recovery

Non-equilibrium thermodynamic processes, such as diffusion, heat transfer and electrical current conduction are characterised by the flow J_k and the thermodynamic force which causes the process Y_k . The Onsager's linear approximation states that N processes are related as

$$J_k = \sum_{j=1}^N L_{jk} Y_j \quad (1)$$

where $L_{jk} = L_{kj}$ are the phenomenological coefficients. The processes can be coupled by non-diagonal components of the matrix L_{jk} . Thus, if one of the processes is diffusion of the polar groups and another is plasma-driven conduction, corresponding flows can be coupled, so that when plasma is turned on a gradient of concentration exists however, no diffusion occurs due to coupling with the electric contraction. The most direct analogy is the thermodiffusion or coupling of diffusion with heat conduction [16]. When plasma is turned off, due to diffusion the polar groups transport themselves into the bulk of the material so that the surface energy is minimised. The process is similar to self-healing of voids and cracks in certain materials, which can be achieved by bringing a damaged material away from the state of equilibrium and coupling the healing forces with those responsible for the relaxation [17].

A number of experimental studies of hydrophobic recovery have been conducted [18–21]. Table 1 summarises the results of experimental studies of hydrophobic recovery for different polymers produced by different research groups. In this table, θ_U is the water CA of untreated surface, θ_0 is the water CA measured immediately after the plasma treatment, and θ_L is the latest measured water CA and R is the recovery percentage. However, no theoretical model of this process has been suggested so far. Below we suggest such a model combining the diffusion, molecular reorientation and wetting.

3. Modelling

The water CA of a solid surface is a function of surface chemistry and roughness. The surface roughness is not changed during the plasma treatment and recovery processes. The change in the water CA can be explained by the change in the surface chemistry only. Such mechanisms as the diffusion of modified polar groups from

Table 1

Experimental data on hydrophobic recovery of plasma treated polymers.

Polymer	θ_U	θ_0	θ_L	R (%) ^a	Reference
PE	119	63	86	58	Ren et al. [15]
	93	51	65	66	Pascual et al. [26]
	89	40	75	28	Sanchis et al. [27]
PP	100	13	51	56	Yun et al. [28]
	86	56	70	53	Morent et al. [14]
PDMS	120	0	90	25	Kim et al. [9]
a-	79	2	40	50	Lee et al. [30]
PS	85	15	42	61	Larrieu et al. [31]
i-PS	90	20	37	75	Larrieu et al. [31]
PET	72	30	46	61	Morent et al. [14]
PMMA	74	39	48	74	Lim et al. [12]
	65	0	65	100	Tsougeni et al. [32]
PTFE	110	38	80	41	Nakamatsu et al. [33]
PU	87	42	52	77	Sanchis et al. [27]
Photoresist	35	6	22	44	Walther et al. [34]

$$^a R = (\theta_U - \theta_L) / (\theta_U - \theta_0) \times 100.$$

the surface to the bulk and the reorientation of modified sections of polymer chain are responsible for the decrease in the surface energy of the plasma treated surface during the hydrophobic recovery. A model describing the change in the composition of the surface then can be combined with a wetting model such as the Cassie model to predict the change in the water CA as a function of recovery time.

3.1. Diffusion model

A diffusion model is proposed below to estimate the concentration of the polar groups during the hydrophobic recovery. Ionised oxygen or oxygen radicals in oxygen plasma, attack the polymer chains to introduce oxygen-containing groups such as the hydroxyl and carboxyl groups. We assume that due to plasma treatment a thin layer (thickness h) of modified molecules is formed on the outmost surface. The initial concentration of modified molecules in this layer is C_0 (Fig. 1a). The driving force for the diffusion is the concentration difference of the polar groups between the modified thin layer and the bulk of the material.

During the recovery process, the modified molecules diffuse into the bulk of the polymer. The concentration of polar molecules in the bulk of the polymer can be expressed as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (2)$$

where C is the concentration of polar molecules, D is the self-diffusion coefficient of modified chains, x is the distance from the surface, and t is the recovery time. If the plasma-treated polymer is assumed to be homogeneous, isotropic, and thick enough, then, for modelling purposes, it can be considered as a semi-infinite solid. The solution to this diffusion problem can be obtained by considering the initial plasma treated layer ($0 < x < h$) as a series of line sources with concentration C_0 . Each line source has a solution in form of exponential function. The final distribution is the sum of these exponential functions, which is in the form of the error function [22]:

$$C(x, t) = \frac{1}{2} C_0 \left\{ \operatorname{erf} \frac{x+h}{2\sqrt{Dt}} - \operatorname{erf} \frac{x-h}{2\sqrt{Dt}} \right\} \quad (3)$$

where the error function $\operatorname{erf}(x)$ is defined as

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2} du \quad (4)$$

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