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The influence of UV-irradiation and support type on surface properties of poly(methyl methacrylate) thin films

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Abstract

Thin poly(methyl methacrylate) (PMMA) films were prepared by a solution casting on different supports (glass and aluminium plates with different gloss). UV-irradiation ($\lambda = 254$ nm) was used for polymer modification. Surface properties of PMMA were studied by contact angle measurements, attenuated total reflection infrared spectroscopy and optical microscopy. It was found that support type has no influence on surface properties of virgin PMMA, however, the changes in these properties were observed during UV modification of polymer film. The most efficient photochemical reactions appeared in sample placed on the rough Al, whereas the smallest effect was observed in polymer on the glass.
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1. Introduction

Surface properties, which are different from bulk properties of polymers, play an important role in many applications. Most of polymers have hydrophobic character, whereas hydrophilicity is needed for reaching a good adhesion to other substances, wettability, printability, etc. [1–3]. Special modification of polymeric surfaces is necessary to get required barrier properties (for instance, reduced permeability), compatibility with another media, proper optical and antistatic properties or light resistance.

In practice, several methods of polymer modification are used to achieve the desired surface properties with unchanged internal structure and then, unchanged bulk properties. For example, flame treatment, corona discharge, plasma modification, electromagnetic radiation (ultraviolet, gamma, X-ray) and ion beams are often applied [2–5].

In recent years, the great progress in understanding surface phenomena and development in their theoretical description was done. Forces occurring on polymer surfaces depend on interactions between macromolecules, which are different inside of material and on the phase boundary. Several reactions occur at the polymer surface during modification such as oxidation, crosslinking, degradation and isomerisation (rotation of functional groups).

There are no direct methods for estimation of the surface free energy of solid polymer (γ_s). It can be obtained from the contact angle measurements. The Young equation describing the three phase equilibrium is usually used:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta \tag{1}$$

where γ_{sv}, γ_{sl} and γ_{lv} are the polymer–vapour, polymer–liquid and liquid–vapour interfacial energies, respectively, and θ is the contact angle. However, the assumption that the spreading pressure, which represents the decrease of solid surface tension due to vapour adsorption may be neglected ($\pi_e \approx 0$), have to be done. In such case $\gamma_s = \gamma_{sv}$ and Eq. (1) can be expressed as

$$\gamma_s = \gamma_{sl} + \gamma_l\cos\theta \tag{2}$$

where γ_l is a surface tension of liquid. The contact angle can be measured by a sessile drop method. It is known that, the

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hydrophilic surface with a high free energy spreads the drop of polar liquid and gives a low contact angle, while the hydrophobic surface with a low free energy gives a high contact angle [1,2].

According to Owens–Wendt method [6], γ_s is a sum of dispersive (γ^d) and polar (γ^p) components of surface free energy:

$$\gamma_s = \gamma^d + \gamma^p \quad (3)$$

and γ_{sl} can be expressed as the geometric mean:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\left(\sqrt{\gamma_s^d \gamma_l^d} + \sqrt{\gamma_s^p \gamma_l^p}\right) \quad (4)$$

where superscripts 's' and 'l' indicate the value for solid and liquid, respectively.

By combining above relationship (4) with Young equation (2) and measurement of contact angle for at least two liquids we can resolve the system of two equations with two unknowns (γ^d and γ^p for polymer). Only the values of γ for test liquids (including polar and dispersive components) have to be known.

The aim of our work was to study the changes of surface properties of poly(methyl methacrylate) thin films (placed on different supports) upon UV-radiation.

PMMA is an important and interesting polymer because of attractive physical and optical properties decisive about its broad application. This is the thermoplastic material with the good tensile strength and hardness, high rigidity, transparency, good insulation properties and thermal stability dependent on tacticity [7–10]. PMMA disadvantages such as brittleness, low chemical resistance can be eliminated by chemical or physical modification. The major uses of PMMA and its composites are motorization, microelectronics, optical accessories, food packages, medicine, dentistry and cosmetics [9–16].

2. Experimental

2.1. Material

Commercial poly(methyl methacrylate) (PMMA, Sigma–Aldrich Chemie GmbH, Germany) was used without any purification. PMMA films are characterized by a high light transparency (90–99%) but ultraviolet transmission depends on the wavelength (carbonyl groups absorb at 270–280 nm).

Thin films were prepared by casting of 2% (w/v) PMMA chloroform solution onto glass (microscopic slide, Medlab Products Sp. z.o.o., Poland) and aluminum plate with different smoothness and gloss (Al-gloss and Al-mat, commercially available packaging foils, produced by Light Metals Plant, Kęty S.A., Poland). After solvent evaporation, specimens were dried in vacuum at room temperature to a constant weight. The thickness of film, measured with the help of Thickness Gauge, Ultrameter A-91 (INCO, Poland), was 30 μm. The surface of supports and PMMA films were observed under the optical microscope with contrast phase (MOTIC DMBI-223).

2.2. Modification

Polymeric films placed on glass or Al support were exposed to low-pressure mercury vapor lamp TUV30 (Philips, Holland) at room conditions (20 °C and air atmosphere). This lamp emits radiation of 253.7 nm wavelength. Intensity of incident light, measured by Il 1400 Radiometer (International Light, USA), was 21.1 mW/cm^2. Surface properties of samples exposed to various doses were examinated.

2.3. Measurements

The static contact angle (θ) was measured by a sessile drop method at constant room temperature (20 °C) using the DSA10 goniometer of Krüss GmbH (Germany), equipped with software for a drop shape analysis. Diiodomethane (analytically pure, UCB, Belgium) and deionized water were applied as the test liquids. The image of liquid drop (volume of 2–3 μl) was recorded by video camera and fitted by means of mathematical functions. Each given θ value is the average of minimum 10 measurements. The precision was 1°. Surface free energies (γ_s) and their dispersive (γ^d) and polar (γ^p) components were calculated by Owens–Wendt method [6]. From θ measurements, also work of water adhesion to PMMA surface was obtained.

ATR-FT-IR spectra were done using Genesis II FT-IR spectrophotometer (Mattson, USA) equipped in ATR device (Miracle™ PIKE Technologies) with zinc selenide (ZnSe) crystal. The number of registered scans was 64, resolution: 2 cm^{-1}.

3. Results and discussion

Surface properties of PMMA films of the same thickness (30 μm) were studied using contact angle measurements and attenuated total reflection Fourier transform infra-red spectroscopy (ATR-FT-IR). Moreover, the quality of polymer surface was observed under optical microscope.

Contact angle (θ) measurement is very sensitive method to surface changes although does not give information about type of groups present. Thus, the identification of functional groups located at the surface was done using ATR-FT-IR. In this method, the electromagnetic wave is reflected at the polymer/crystal surface because of differences in the refractive index in both substances. It penetrates only a small distance into the sample, where is partly absorbed. For example, the penetration depth, calculated for wavelength of 5800 nm (i.e. 1724 cm^{-1}, at which ester groups from PMMA absorb), is 843 nm.

PMMA films, prepared by a solution casting on aluminium (with different gloss) and glass support, do not exhibit any visual differences. All samples were smooth, transparent, without any defects. ATR-FT-IR spectra of unmodified PMMA films also do not show differences, which means that the chemical structure on sample surface is the same. It is understood because the film obtained is much thicker than monolayer (deduced on the base of gyration radius = 0.5 μm in

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