



# Surface studies of UV-irradiated poly(vinyl chloride)/poly(methyl methacrylate) blends



Jolanta Kowalonek

Faculty of Chemistry, Nicolaus Copernicus University in Toruń, Gagarina 7, 87-100 Toruń, Poland

## ARTICLE INFO

### Article history:

Received 16 December 2015

Received in revised form

6 August 2016

Accepted 16 September 2016

Available online 16 September 2016

### Keywords:

Polymer blends

PVC

PMMA

UV-irradiation

Surface free energy

AFM

## ABSTRACT

Surface properties of poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA) and their blends have been studied using FTIR-ATR spectroscopy, AFM and contact angle measurements. It was found that the surfaces of PVC/PMMA blends were enriched in PMMA, the lower surface free energy component. The results also revealed the existence of weak interactions between the blend components resulting in partial miscibility of system observed for the blends containing below 40% of PMMA.

UV-irradiation made the sample surfaces more polar and rough owing to photochemical processes such as oxidation, degradation, dehydrochlorination, depolymerization or etching. The oxidation was more efficient for PVC compared to PMMA. In the case of PVC/PMMA blends, the efficiency of oxidation reactions increased with increasing PVC content and this process was approximately the average of the changes in the pure polymers. The photooxidation reactions were accompanied by degradation reactions leading to formation of low molecular weight oxidized products.

AFM studies of UV-irradiated sample surfaces revealed cone-like and globular objects which were easily removed from the surfaces after washing the samples. These objects were made of low molecular weight oxidized material and/or methyl methacrylate. Only neat PMMA surface behaved contrary to all samples. It seemed that irradiation did not yield any changes in surface morphology of PMMA but washed surface of this polymer revealed presence of cone-like structures. It suggests that the mechanism of photooxidative degradation of pure PMMA and PMMA in the blends was different. Probably the presence of chlorine radicals from PVC modifies the route of PMMA photochemical processes in PVC/PMMA blends.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introductions

Blending of polymers is a method of obtaining new materials with properties different from properties of individual components. The main goal of blending is to improve bulk properties, especially thermal and mechanical. Polymers forming such blends are called compatible, which is a technological term. The compatible blends are often immiscible or partially miscible, which manifests in phase separation in a bulk and also at the surface region. Single phase behavior in a microscopic scale is characteristic of miscible blends. Such miscibility occurring at the molecular level is due to the interactions between components. However, polymer immiscibility is more common phenomenon than miscibility [1–6].

Interactions between polymers in the bulk affect surface composition and morphology of the polymer blend films. Moreover, many other factors such as component ratio, type of solvent,

crystallinity, preparation conditions (time and temperature) and surface free energy of components influence the surface composition and morphology of polymeric blends [5,6]. The lower surface energy component enriches the blend surface, which suggests phase separated structure. Consequently, bulk and surface compositions are different very often [5–8]. Moreover, physical features of the sample outer layers vary from these in the bulk. Density of the sample is lower in the outer layer. The mobility of side-groups, macromolecule segments or even the whole macromolecules is greater at the surface compared to that in the bulk. Reorientation of side-groups or chain segments is important property related to the ability to adjust the surface to the surrounding environment to acquire the lowest energy. Such ability is useful in studies of wetting phenomena, for example in adhesion processes, printing, waterproofing [9]. Thus, surface studies provide valuable information on the surface structure.

The investigations of photochemical processes of polymer blends require attention. In general, UV radiation together with

E-mail address: [jk@chem.umk.pl](mailto:jk@chem.umk.pl).

oxygen induces oxidation, degradation, crosslinking and formation of volatile and gaseous products in polymers. Although these processes are well understood for pure polymers, however, in polymer mixtures the photochemical reactions can be hampered or accelerated compared to these processes in unmixed polymers [10–12].

Photooxidative degradation of polymer blends depends on the photostability of blend components, polymer miscibility, blend composition and blend surface composition. A surface is the place where any photochemical changes start and then they gradually come into the bulk of the material [10,13,14]. Thus, the surface composition of the blends determines their behavior under UV-radiation.

UVC radiation is not naturally present on Earth, however can be artificially produced. This short-wave energetic radiation is widely used in medicine or food industry as a sterilizing factor to improve microbiological purity of the equipment or product, for instance, it is used for disinfection of medical and cosmetic devices, in food industry it is used for cleaning contaminated tools, conveyor belts, packaging or even larger surfaces made of polymers [15]. The devices, equipment, tools, etc. in medicine or food industry are often made of polymers. From this point of view, it is vital to check the photostability of such materials.

The purpose of this work was to study the photochemical processes at PVC/PMMA blend surfaces using FTIR-ATR spectroscopy, AFM and contact angle measurements. These blends were studied in terms of miscibility [16–23], thermal degradation [24–29] or conductivity [16,17,30–32]. The miscibility of these polymers is not obvious as some published results indicate the miscibility of PVC with PMMA over the entire composition range [16–19,22,23] but other - partial miscibility of the components up to 60% of PMMA in the blends [20,21]. The difference may result from the use of polymers having different molecular weights and different sample preparation methods. Miscibility in this system can be explained by interactions occurring between carbonyl group of PMMA and hydrogen atom from H–C–Cl group of PVC (hydrogen bond), or between carbon atom from carbonyl group of PMMA and chlorine atom from Cl–C–H group of PVC (dipole-dipole interaction) [16–23].

Moreover, research on surface composition of these mixtures was also conducted [33–40]. It was stated that the surface region of PVC/PMMA blends, cast from tetrahydrofuran, was enriched in PMMA [33–38], but these blends, cast from methyl ethyl ketone, were homogenous and the surface composition was in accordance with the bulk composition [33].

However, changes in surface properties of PVC/PMMA blends upon UV-irradiation were not investigated until now. Thus, this article includes a description of photochemical alterations taking place on the surfaces of PVC/PMMA mixtures. The mechanism of photoprocesses in the blends is deduced on basis of the known mechanisms of photooxidative degradation of the homopolymers.

## 2. Material and methods

Poly(vinyl chloride) (PVC) ( $\overline{M}_w = 97,000$ ) and poly(methyl methacrylate) (PMMA) ( $\overline{M}_w = 120,000$ ) were purchased from Aldrich. 4% (m/v) basic solutions of these polymers were prepared by dissolving PVC in tetrahydrofuran and PMMA in toluene. Then, 2% (m/v) solutions of polymeric blends of different weigh ratios of the components were obtained by mixing proper volumes of the basic polymeric solutions.

Thin polymeric films were obtained by casting 2% (m/v) solutions onto the levelled glass plates. After solvent evaporation, films were dried to a constant weight at 40 °C in vacuum. The film thickness was about 30  $\mu\text{m}$ –40  $\mu\text{m}$ .

Irradiation was conducted with a low pressure mercury vapor lamp (TUV 30 W, Philips, Holland) emitting light with a wavelength

of 254 nm. The intensity of incident light, measured with electronic radiometer HD 9021 (Delta OHM, Italy), was 19.9 W/m<sup>2</sup>.

FTIR-ATR spectra of PVC/PMMA films were collected using FTIR Genesis II (Mattson, USA) spectrophotometer equipped with ATR (Pike Technologies, Inc.) containing ZnSe crystal. FTIR-ATR spectra were recorded at a resolution of 4 cm<sup>-1</sup> with a scan number of 64, while transmission FTIR spectra were collected at 2 cm<sup>-1</sup> resolution and 32 scans.

Contact angles, surface free energy and its components were gained using a DSA G10 goniometer (Krüss GmbH, Germany). A drop of water or diiodomethane was placed onto a sample surface with microsyringe and the value of contact angle was calculated by the computer on the basis of the obtained image of the liquid drop. Measurements of contact angles were made for untreated and UV-treated samples. The value of contact angle was average of ca. 8 measurements and the deviation from the average was within  $\pm 2$  deg. All measurements were carried out at room temperature.

AFM images were obtained with MultiMode NanoScope III, Veeco Metrology Inc. (USA) with silicon probe (Veeco) in tapping mode in air, at room temperature. The most typical images were chosen for presentation, additionally roughness parameters ( $R_a$  - an arithmetic mean, and  $R_q$  - a root mean square) were calculated for scan area 5  $\mu\text{m}$   $\times$  5  $\mu\text{m}$ .

These experiments were also conducted for washed samples. For this purpose, the UV-irradiated samples were immersed in deionized water for 5 min and then dried under vacuum at 50 °C during 48 h. Such a procedure was possible as both polymers are insoluble in water.

## 3. Results and discussion

### 3.1. Untreated PVC, PMMA and PVC/PMMA blends

FTIR-ATR method was applied to study the surface composition of PVC/PMMA blends. The intensity of the ATR spectra depends on the penetration depth of the wave into a sample. The penetration depth ( $d_p$ ) is expressed by the following equation [33,43]:

$$d_p = \frac{\lambda}{2\pi n_c \left[ \sin^2 \theta - (n_s/n_c)^2 \right]^{1/2}} \quad (1)$$

where:  $\theta$  - the incidence angle (for ZnSe - 45°),  $n_c$  - the refractive index of the crystal (2.4),  $n_s$  - the refractive index of the sample (1.5),  $\lambda$  - the wavelength of light.

As  $\theta$ ,  $n_c$ ,  $n_s$  are invariable in this experiment, the penetration depth depends on  $\lambda$  or  $\bar{\nu}$ , so the depth of penetration is about 0.5  $\mu\text{m}$ , 1.17  $\mu\text{m}$ , and 3.34  $\mu\text{m}$  at 4000 cm<sup>-1</sup>, 1720 cm<sup>-1</sup> and 600 cm<sup>-1</sup>, respectively. At 1720 cm<sup>-1</sup>, we study about 3% of the surface layer of the film. Using the ATR software, we can process the spectra and obtain corrected spectra as if they would be collected for the same penetration depth.

Fig. 1a shows FTIR-ATR spectra of PVC, PMMA and their blends in the range of 1800–600 cm<sup>-1</sup>. It is seen that most of the spectra of the polymeric blends is similar to pure PMMA, only PVC/PMMA (80/20) spectrum is similar to pure PVC, which may suggest that more PMMA is present in the surface region of PVC/PMMA blends. Also absorptivity of PVC is lower than that of PMMA, which makes the detection of PVC difficult [33]. In Table 1 there are maxima of absorption bands of PVC, PMMA and the blends. Slight band shifts are seen for the blends with 80–60% of PVC, while for the blend with 80% of PMMA the band shifts are within the measurement error. Thus, the maximum of absorption band at 1725 cm<sup>-1</sup> assigned to vibrations of carbonyl groups [17,22,23,41,42]

Download English Version:

<https://daneshyari.com/en/article/5200983>

Download Persian Version:

<https://daneshyari.com/article/5200983>

[Daneshyari.com](https://daneshyari.com)