AFM investigation of poly(vinyl chloride)/poly(vinyl acetate) blends

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Abstract

The blending (mixturing) of two polymers - Poly(vinyl acetate) (PVAC) and Poly(vinyl chloride) (PVC) was carried out. These blends, as well as their radiation stability, were investigated using AFM method.

Introduction

Blending of polymers is economic way to obtain new materials with specific properties without the need to synthesis, which is usually energy and time consumed process. In industry few different techniques are used for blend or alloy production such as dry mixing (in room or higher temperature), precipitation process and sinter, however, in laboratory practice, the solution blending is often applied. The component miscibility (or immiscibility) and ratio as well as conditions of preparation strongly affects the blend morphology, which decides about many its properties [1,2].

Commercial vinyl polymers such as poly(vinyl chloride) (PVC) or poly(vinyl acetate) (PVAC) are extensively studied because of their broad applications in industry. PVC is mainly used as construction material, rigid pipe, flooring, wire and cable insulation, housewares, packaging films and sheets. Major uses of PVAC are water-based paints, adhesives, and substrate for poly(vinyl alcohol) production [3]. The polymer blending can leads to obtaining a new materials joining the properties of both components. However, some physico-chemical properties of polymer in blend are unpredictable and non-additive. In numerous cases the synergism or antagonism of properties is observed.

It has been previously reported using FTIR and UV-VIS spectroscopy that addition of small amount of PVAC to PVC films influences its photostability. During our previous studies of polymer blends exposed to UV-irradiation we found that the lot of factors influences the course of their photodegradation [4-6]. Very important factors are polymer miscibility and blend morphology which can be observed using SEM [7] or AFM [8]. It must be mentioned that AFM method was widely used for investigation of polymers topography and surface features [9] and for investigation of radiation defects in polymers [10].

The aim of this work is investigation of PVC/PVAC blending and these blends changing during UV-irradiation.

Experiment

The blends with different composition (1%, 5%, and 10% PVAC) were prepared by mixing of PVC and PVAC solutions. For this purpose PVC produced by Anwil (Wloclawek, Poland)
and PVAC supplied by Fluka were dissolved in solvent mixture (1,2-dichlorobenzene and tetrahydrofuran, volume ratio 1:1). 2% polymer solutions of PVC and PVAC were mixed and cast onto leveled glass plates. After solvent evaporation, samples were dried in vacuum at room temperature to a constant weight. Thin films were used for photodegradation studies.

The low pressure mercury lamp (TUV 30W, Philips, Holland) as a source of UV-radiation was used. The radiation wavelength 254 nm, light intensity at sample level was 2.35mW/cm\(^2\). The samples were irradiated 10 hours from both sides (together 20 hours) at room temperature and in air atmosphere.

Changes of surface morphology were tested using AFM (Solver P47, NT-MDT), working in tapping regime (Si-cantilevers, frequency approx. 250 kHz).

Results and discussions

AFM images demonstrates that the side “from glass” is more flat and smooth (it is mainly replica of glass surface) contrary to free side contacted only with air. However, even on this smooth side it can be seen non-miscibility polymers in blends with different composition.

The Table demonstrates the roughness of different samples in nanometers:

<table>
<thead>
<tr>
<th>Side</th>
<th>Sample</th>
<th>pure PVC</th>
<th>1%PVAC</th>
<th>5%PVAC</th>
<th>10%PVAC</th>
<th>pure,non-irrad.</th>
</tr>
</thead>
<tbody>
<tr>
<td>“top”</td>
<td></td>
<td>8</td>
<td>1.8</td>
<td>3.3</td>
<td>4.5</td>
<td>1.1</td>
</tr>
<tr>
<td>“bottom”</td>
<td></td>
<td>2.1</td>
<td>1.1</td>
<td>1.5</td>
<td>2.7</td>
<td>1.1</td>
</tr>
</tbody>
</table>

It is seen that in samples with small amount PVAC added to PVC the roughness increases with the concentration of PVAC (from 1% to 5%). The added polymer (PVAC) forms small inclusions which size can be estimated approximately from 50 nm to 100 nm. (see Fig.1)

The higher amount of PVAC (10%) shows another structure: in this case PVAC forms larger domains (like islands on AFM images) and both non-miscible but more flat phases co-exist.

After exposure of samples to UV some surface defects appeared on polymer surface. Small crazes, cracks and voids are seen in Fig.2 It can be explained by efficient photodegradation process during which the polymer chains efficiently break. Small voids occur resulting of evaporation of low-molecular, volatile degradation products from polymer bulk. Generally, UV-irradiation cause increase of roughness and it was explained as etching of surface (by removing of some loosely joined molecules).

UV-irradiation of pure PVC leads to much higher surface roughness comparing to irradiation of PVC + PVAC blends. We can conclude that the etching of pure PVC is more efficient that etching of the blends. It is in agreement with our previous results obtained on the base of spectrophotometric measurements (FTIR, UV-VIS). We found that PVAC added in small amount (1-5%) hampers photooxidative degradation of PVC.

Conclusions

The results obtained demonstrates the efficiency of AFM method for studying of morphology and amorphous polymer blend surfaces. It can be also succesfuly used for the monitoring of
photodegradation processes in such compositions.

It was found that addition of 1-10% amount of PVAC to PVC leads to formation of small particles non-uniformly distributed in matrix of major component. The reason of such behaviour is unmiscibility of PVC and PVAC and phase separation during film formation. The surface morphology of films obtained by solution casting onto glass plate is dependent on the sample side. Surface from the glass side is relatively smooth and changes upon UV-irradiation are negligible. The greater changes caused by UV were observed on more rough surface which was only in contact with air during solvent evaporation.