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# Surface modification of polypropylene substrates by UV photografting of methyl methacrylate (MMA) for improved surface wettability

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## Abstract

Despite polypropylene is one of the most used commodity plastics, its adhesion properties are remarkably restricted by its non-polar nature which leads to low wetting properties and, consequently, poor adhesion behavior. We report the use of ultraviolet photografting process of methyl methacrylate (MMA) monomer as an efficient chemical treatment for surface activation of polypropylene. Contact angle measurements are used for evaluating changes in polypropylene wetting properties together with surface free energy calculations. Chemical changes are showed in terms of the exposure time to UV radiation. Scanning electron microscopy (SEM) has been used to evaluate topography changes in a qualitative way; atomic force microscopy (AFF) has been used for a quantitative evaluation of surface changes in terms of roughness. The use of Fourier transformed infrared spectroscopy (FTIR) has revealed the nature of the chemical changes induced by the photografting process of MMA.

**Keywords:** photopolymerization, poly(propylene) (PP), surface modification, functionalization of polymers.

## 1. Introduction.

Polypropylene is one of the most used commodity plastics as a consequence of a good balance between properties (mechanical, thermal, chemical, processing, etc.) and cost. From a chemical point of view, it shows high inertness due to its non-polar nature and this leads to a hydrophobic polymer characterized by very low wetting properties. This fact is mainly responsible for problems in adhesion, painting, coating, etc. So that, the use of polypropylene in these applications requires a surface pre-treatment in order to improve its intrinsically low wetting properties. This can be achieved by insertion of polar groups and promoting changes in surface topography.

It is possible to modify the bulk properties of polymers by blending with different polymers or using reactive extrusion processes with the aid of compatibilizing agents. Blends of polypropylene with polar polymers such as ethylene-acrylic acid are useful to obtain a remarkable increase in hydrophilic behavior and this contributes to improve adhesion properties.[1] Nevertheless, surface modifications are preferable for surface adhesion. There are several chemical and physical processes for surface modification. Physical processes as plasma technologies [2-4] (corona, low pressure, atmospheric plasma, etc.) are very useful to achieve good functionalization levels together with interesting changes in surface roughness, but it is important to remark that these techniques are still expensive. On other hand, chemical processes are characterized by easy implementation and low cost and the overall effects are similar to those obtained with plasma processes. Some of these chemical processes are based on the use of strong acids or alkalis to promote surface activation and/or changes in surface roughness. In addition to the use of these aggressive chemicals, it is possible to achieve surface activation of a wide variety of monomers by interlocking of polar groups on polypropylene chains and this fact, will also promote changes in surface roughness.

1 This can be carried out by using a UV induced grafting process [5-8]. This requires the  
2 use of a base monomer, such as acrylic, which can be activated by UV radiation in the  
3 presence of a free radical photoinitiator which decomposes rapidly [9]. The action of  
4 UV light leads the photoinitiator to an excited state which needs hydrogen to form  
5 stable free radicals (Scheme 1).  
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### 11 **Scheme 1**

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19 Then hydrogen abstraction from the topmost layers of the polymer occurs thus  
20 leading to formation of interlock points in which, monomer can be chemically bonded  
21 by addition processes. These free radicals derived from photoinitiator and polymer  
22 chains at the topmost surface layers can react with the acrylic monomer to form typical  
23 species of an addition process as indicated in Scheme 2 so that, new radicals are formed.  
24 Addition processes continue until termination occurs. After termination, some  
25 macroradical are chemically grafted to the topmost layers of the polymer surface and  
26 also, some non-grafted oligomers can be obtained (Scheme 3). These oligomers must  
27 be removed by cleaning surfaces after the UV grafting process.  
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### 43 **Scheme 2**

### 44 **Scheme 3**

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51 In a typical photografting process, the monomer is dissolved in a carrier solvent  
52 such as acetone, benzene, chloroform, methanol, etc. together with the appropriate  
53 amount of the photoinitiator. Some authors have used these processes to modify  
54 filtration properties on analytical membranes. [10-14]. Other research works have  
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1 focused on the use of UV photografting processes as coating for electrolytic copper.  
2 [15] Photografting processes with different base monomers have been successfully used  
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4 to improve hydrophilic nature of electroactive polymers such as polyaniline and in some  
5  
6 cases, self-protonated surfaces are obtained thus having a positive effect on surface  
7  
8 conductivity.[16]  
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11 The photografting process can be carried out in a single stage or in a double step  
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13 process [7, 17]. The use of a single stage process is preferable since it lowers the  
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15 working time which is a key factor for industrial applications. In this, the polymer  
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17 surface is exposed to UV radiation in the presence of a solution containing both  
18  
19 monomer and photoinitiator. The use of different photoinitiators such as benzophenone  
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21 (BP) [18], methylbenzoylformate (MBF), xanthone, etc. has been reported with  
22  
23 excellent results since all of them show absorption peaks in the UV range. With respect  
24  
25 to solvent, it is important to remark that it must be appropriately selected to ensure good  
26  
27 solubility of both the photoinitiator and the monomer. The most commonly used  
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29 solvents are acetone, methanol, chloroform, carbon tetrachloride, cyclohexane,  
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31 cyclohexanone, ethyl acetate, tetrahydrofuran, etc. and mixtures, depending on the  
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33 monomer and/or the photoinitiator. [19, 20] Some results about the optimum  
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35 photoinitiator/monomer ratio with several solvents have been reported and they have  
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37 great influence on final grafting of the monomer on the polymer surface.  
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46 Regarding the use of monomers, a wide variety of compounds have been used  
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48 by different authors with different purposes. Some monomers such as polyacrylamide  
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50 (PAAm) [21], polyacrylic acid (PAA) [21], vinyl acetate (VAc) [22-24], etc. are used to  
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52 improve and/or control wettability on chemically inert polymers for improved adhesion,  
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54 as we have reported in our previous works with acrylic acid (AA) [25] and methyl  
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56 methacrylate [25]. Trimethylolpropane triacrylate has been used to provide good  
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1 thermal degradation resistance [26] and 1,6-hexanediol diacrylate to enhance  
2 mechanical and physical properties of jute fibers [27]. Different acrylic monomers have  
3  
4 been used to improve interface phenomena between the polymeric matrix and  
5  
6 reinforcements in composite materials.[28, 29] The use of other hydrophobic monomers  
7  
8 can lead to super-hydrophobic properties for self-cleaning materials. For example,  
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10 polyacrylic acid (PAA) can be grafted onto Nylon-6 fibers to form PAA hydrogels  
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12 which are useful to avoid seaweeds' adhesion on fishnets. [30] Some works have  
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14 reported the usefulness of polyvinylpyrrolidone-iodine to provide antibacterial  
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16 properties on polymer substrates [31]; different kinetic studies on grafting isobornyl  
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18 acrylate have been carried out as this monomer is suitable as coating for digital HD-  
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20 DVD [32, 33].  
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26 In this work we have used a one-step UV photopolymerization process of methyl  
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28 methacrylate (MMA) monomer in presence on benzophenone (BP) as photoinitiator on  
29  
30 an acetone solution to increase the low intrinsic wettability of polypropylene sheets in  
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32 order to provide good wetting properties for different technological processes such as  
33  
34 adhesive bonding, painting, etc. The influence of the exposure time to UV radiation has  
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36 been evaluated and the overall changes in surface wettability have been studied by  
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38 contact angle measurements and subsequent free energy calculation. A qualitative  
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40 analysis of surface changes has been carried by using scanning electron microscopy  
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42 (SEM) and quantitative information has been determined by using atomic force  
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44 microscopy (AFM). Chemical changes derived from the surface pre-treatment have  
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46 been followed by FTIR-ATR.  
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## 58 **2.- Experimental**

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## **2.1.- Materials.**

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2 Photografting process was carried out on a polypropylene commercial grade  
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4 ISPLEN ® PB 180 G2M provided by Repsol YPF (Repsol, Madrid, Spain). This is a  
5  
6 heterophase copolymer with high fluency which is appropriate for injection molding  
7  
8 with a flow rate of 20 g/10 min and a density of 0.905 g/cm<sup>3</sup>. Sheets sizing 160x60x2.2  
9  
10 mm<sup>3</sup> were injection molded at a temperature of 230 °C with a Mateu&Sole, model  
11  
12 Meteor 270/75 (Mateu&Sole, S.A., Barcelona, Spain). After injection molding, samples  
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14 sizing 10x10 mm<sup>2</sup> were cut with a hydraulic press Melchor Gabilondo, model KCK-  
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16 15A (Melchor Gabilondo S.A., Vizcaya, Spain). These samples were washed in double  
17  
18 distilled water to remove impurities and then they were stored in a vacuum desiccator.  
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24 As a base monomer for surface modification, stabilized methyl methacrylate  
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26 (MMA) monomer with a purity of 99% was used (Acros Organics, Geel, Belgium). The  
27  
28 selected photoinitiator was benzophenone (BP) supplied by Scharlau Chemie S.A.  
29  
30 (Scharlab S.L., Barcelona, Spain). Both monomer and photoinitiator were dissolved in  
31  
32 laboratory grade acetone (Aurelio Crespo Sospedra, C.B. Alfafar, Valencia, Spain) to  
33  
34 obtain the base solution for UV photografting process with a MMA:acetone volume  
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36 ratio of 1:4. After this, 5 weight % of benzophenone was added.  
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## **2.2.- Photopolymerization process.**

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44 A pressure mercury lamp (1000 W and 350 nm by wavenumber) mounted on a  
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46 UVASPOT 1000RF2 supplied by Honle UV Technology (Honle Spain, S.A.,  
47  
48 Barcelona, Spain) was used for surface modification.  
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53 In a first step samples sizing 10x10 mm<sup>2</sup> are placed in a Petri dish and fully  
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55 covered by the solution containing MMA monomer and benzophenone. Then the Petri  
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57 dish is covered with a glass lid to guarantee invariable atmosphere conditions avoiding  
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1 gas emanation. After this, the Petri dish was placed on aluminium rack which is located  
2 at a fixed distance of 25 cm below the mercury lamp. The exposure time to UV  
3 radiation was varied between 30 up to 240 s and after exposure to UV radiation samples  
4 were washed with distilled water to remove non-grafted monomer, oligomers and  
5 volatiles and, finally, dried at room temperature in a vacuum desiccator.  
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### 11 **2.3.- Wettability characterization and surface free energy calculation.**

12 Contact angle measurements were carried out with a EasyDrop Standard  
13 goniometer model FM140 (KRÜSS GmbH, Hamburg, Deutschland) which is equipped  
14 with a video capture kit and analysis software (Drop Shape Analysis SW21; DSA1).  
15 Four different test liquids were used as test liquids: diiodomethane (stabilized, >99%  
16 purity) supplied by Acros Organics (Acros Organics, Geel, Belgium), formamide  
17 (reagent grade ACS), and glycerol (> 99% purity) supplied by Scharlau Chemie S.A.  
18 (Scharlab S.L., Barcelona, Spain) and double distilled water. At least ten measurements  
19 were carried out for each sample and average values were calculated. The maximum  
20 error did not exceed 3%. Surface free energy values were calculated using the Owens-  
21 Wendt method which takes into account the dispersive (non-polar) and polar  
22 contribution to the total surface free energy value.[25]  
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### 46 **2.4.- Surface morphology.**

47 Surface morphology of low density polyethylene sheets pre-treated with UV  
48 photografting process were evaluated with a scanning electron microscope SEM,  
49 supplied by FEI, model PHENOM (FEI Company, Eindhoven, The Netherlands), with  
50 an accelerating voltage of 5KV. Samples were covered with a gold-palladium alloy in a  
51 Sputter Coater EMITECH mod. SC7620 (Quorum Technologies Ltd, East Sussex, UK).  
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Micro-scale roughness study was carried out with a portable surface roughness tester SurfTest SJ-301 (Mitutoyo, Hampshire, United Kingdom) with a profile filter  $\lambda c$  of 0.8 mm and average roughness (Ra) and height of average roughness (Rz) were calculated for a total length of 3.2 mm.

Surface topography changes were evaluated with atomic force microscopy (AFM) using a Multimode AFM microscope with a Nanoscope IIIa AD/CS controller (Veeco Metrology Group, Cambridge, UK). A monolithic silicon cantilever NanoWorld Point-robe<sup>®</sup> (NCH) with a force constant of 42 N m<sup>-1</sup> and a resonance frequency of 320 Hz was used to work on the tapping mode.

## 2.5.- *Characterization of chemical changes.*

Chemical changes produced by the surface pre-treatment by photopolymerization were studied using Fourier transformed infrared spectroscopy (FTIR) with attenuated total reflectance (ATR) accessory. The FTIR spectrometer was a Perkin Elmer, mod FTIR Spectrum BX (PerkinElmer España, S.L., Madrid, Spain) and the ATR accessory model was MIRacle supplied by Pike Technologies (PIKE Technologies, Inc. , Madison , USA). Samples were directly placed in the ATR accessory and 10 scans were performed in the 4000 – 800 cm<sup>-1</sup> wavenumber range with a resolution of 2 cm<sup>-1</sup>.

## 3.- **Results and discussion.**

### 3.1.- *Characterization of wettability and chemical changes.*

Surface changes due to methyl methacrylate photopolymerization were followed by contact angle measurements with different test liquids. Figure 1 shows a plot

1 evolution of the static contact angle of polypropylene using different test liquids in  
2 terms of the exposure time to UV radiation in presence of the monomer solution and  
3 photoinitiator. We can observe a remarkable decrease in contact angle values for all the  
4 test liquids. In the case of water a test liquid, the initial contact angle of untreated  
5 polypropylene is about 100°. We can see that this contact angle is considerably reduced  
6 up to values of about 47° for an exposure time of 90 s. As the exposure time increases  
7 over 90 s, the contact angle follows similar tendency but more slightly up to values  
8 close to 40° for exposure times of about 210 s. Similar tendency can be seen with the  
9 other three test liquids. Regarding glycerol as test liquid, an initial decrease in contact  
10 angle values is detected for exposure times of 90 s and once reached this time, the  
11 decrease in contact angle is less pronounced. With respect to the use of diiodomethane  
12 as test liquid, the initial contact angle, located at 54°, is rapidly decreased up to values  
13 of 37° for an exposure time of 30 s and after this, a slight decrease up to values of 30°  
14 for exposure times in the 120- 180 s range is observed. Finally, the initial contact angle  
15 of formamide, located at 71.4° is remarkably decreased up to values of about 47° for an  
16 exposure time of 30 s and a slight decreasing tendency is observe with increasing times.  
17 It is important to remark that the surface pre-treatment with MMA does not lead to total  
18 wettability (in the exposure time range evaluated in this research work), since contact  
19 angles for all liquids remain at values higher that 0°, but a great decrease is obtained for  
20 the four test liquids as observed in Figure 1 and this would have a positive effect on  
21 wetting properties of polypropylene substrates.  
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### 53 **Figure 1**

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As we have described previously, the use of four different test liquids allows the use of the Owens-Wendt method to estimate changes in the solid surface energy values. Furthermore, the use of this method allows estimating the polar ( $\gamma_s^p$ ) and dispersive ( $\gamma_s^d$ ) contributions to total surface energy ( $\gamma_s$ ) as it can be observed in Table 1. As we can see, untreated polypropylene is characterized by a relatively low surface energy value of about  $31.5 \text{ mJ m}^{-2}$ , with a low polar contribution ( $3.1 \text{ mJ m}^{-2}$ ) as a consequence of its non-polar nature. For short exposure times to UV radiation in presence of MMA monomer and initiator solution in acetone (30 s) we can see a remarkable increase in surface energy up to values of  $42.2 \text{ mJ m}^{-2}$ , with a slight increase in the polar contribution. As the exposure times increases, we observe a noticeable increase in the polar contribution (from  $3.1 \text{ mJ m}^{-2}$  for the untreated polypropylene up to values in the  $24 - 26 \text{ mJ m}^{-2}$  range for exposure times longer than 150 s). Regarding the dispersive contribution, it is important to remark that it remains with values in the  $26 - 30 \text{ mJ m}^{-2}$  range for almost all the exposure times. These results are representative for a functionalization process of the polypropylene surface by insertion of polar groups derived from methyl methacrylate (MMA) monomers which are chemically bonded to polypropylene surface during the photopolymerization process. The total surface energy of polypropylene is increased from  $31.5 \text{ mJ m}^{-2}$  which is representative for low wetting properties, up to values around  $52 - 56 \text{ mJ m}^{-2}$  (for exposure times in the 150 – 210 s) which are interesting values for wetting processes such as adhesion bonding.

### Table 1

FTIR is a useful technique to evaluate chemical changes in the topmost layers as a consequence of methyl methacrylate photografting on polypropylene surface. As we

1 have described previously, presence of an initiator and subsequent exposure to UV  
2 radiation, leads to formation of interlock points in which, activated MMA monomers  
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4 can be chemically bonded to polypropylene chains; so that, the grafted monomer is not  
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7 lost after washing.  
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## 10 11 12 **Figure 2** 13 14 15

16  
17 Figure 2 shows a comparative plot of the FTIR-ATR spectra for different  
18 polypropylene surfaces subjected to different exposure times to MMA photografting. As  
19 we can observe, treated samples show presence of different peaks and bands that do not  
20  
21 appear in the untreated polypropylene surface. These peaks are directly related to  
22 presence of interlocked methyl methacrylate monomers on top most layers. Presence of  
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24 -C=O species can be detected in the pre-treated samples as different typical absorption  
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26 peaks can be seen at  $1649\text{ cm}^{-1}$  and  $1729\text{ cm}^{-1}$ . In addition, presence of ester groups is  
27  
28 evident from the presence of different absorption peaks located at  $1274\text{ cm}^{-1}$ ,  $636\text{ cm}^{-1}$   
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30 and  $1195\text{ cm}^{-1}$ , the last one corresponding to the O-CH<sub>3</sub> group. Furthermore, the  
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32 appearance of different peaks in the untreated polypropylene surface changes as the  
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34 exposure time to MMA photografting increases and this is related to surface chemical  
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36 changes due to chemical bonding of MMA monomers onto polypropylene surface.  
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38 Thus, the peak located at  $1439\text{ cm}^{-1}$ , which corresponds to CH<sub>3</sub> changes in a remarkable  
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40 way due to anchorage or MMA groups. [34]  
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### 53 **3.2.- Characterization of surface morphology.** 54

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56 To analyze the surface changes of polypropylene samples treated with UV  
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58 photografting process of methyl methacrylate, scanning electron microscopy (SEM)  
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1 was used. Figure 3 shows the microphotographs of polypropylene with different exposure  
2 times to UV radiation in presence of MMA monomer together with the corresponding  
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4 water contact angle photograph.  
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### 9 **Figure 3**

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14 The microphotograph for the untreated PP (Figure 3a) is characterized by a very  
15 smooth surface, free of any roughness; thus the initial water contact angle is high,  
16 around 87.3°. As the exposure time to UV photografting increases, we observe  
17 remarkable changes in surface topography. So that, polypropylene subjected to UV  
18 photopolymerization process with an exposure time of 180 s (Fig. 3d) presents a very  
19 rough surface, with large differences in height between the peaks and valleys. This  
20 roughness is closely related to the increase in surface energy produced as a result of the  
21 deposition of a chemically bonded functionalized layer. SEM microphotographs with  
22 different exposure times (60 and 120 s; Figure 3b and 3c respectively) are also shown.  
23  
24 In these cases, there is also a rough surface, but not as much as in the case of 180 s. We  
25 observe rough surfaces but differences in height between peaks and valley seem to be  
26 lower. Also we can observe the importance of surface changes in overall wettability of  
27 polypropylene substrates as the water contact angle decreases with rougher surfaces  
28 together with presence of functionalized species chemically bonded to the top most  
29 layers.  
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51 In addition to this, a micro-roughness study has been done to evaluate changes in  
52 roughness values as a consequence of the UV photografting process. Fig. 4 shows a  
53 comparative plot of the roughness profiles obtained for untreated polypropylene and  
54 polypropylene surfaces with different exposure times to UV photografting process. We  
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1 can observe in a clear way the tendency as the roughness is more pronounced for long  
2 exposure times to UV photografting process. These roughness profiles are in accordance  
3 with previous results regarding surface characterization by SEM techniques and changes  
4 in wetting properties as the main mechanisms responsible for the wettability  
5 improvement are surface functionalization by insertion of polar groups (derived from  
6 methyl methacrylate monomers) and changes in topography due to formation of a  
7 heterogeneous polymer layer in polypropylene surface. In addition to this qualitative  
8 information, Table 2 summarizes the main parameters regarding surface roughness for  
9 untreated and UV photografted polypropylene. The initial average roughness (Ra) of  
10 untreated polypropylene is about 0.11  $\mu\text{m}$  and this value increases as the exposure time  
11 to UV photografting process increases and higher values of Ra are obtained for  
12 exposure times of 240 s (Ra values of about 0.53  $\mu\text{m}$ ). In a similar way, the Rz values,  
13 representative for the height of the average roughness values, we observe an increasing  
14 tendency. So that, the initial Rz value for untreated polypropylene is close to 0.89  $\mu\text{m}$   
15 and this increases up to 3.36  $\mu\text{m}$  for polypropylene surfaces with an exposure time to  
16 UV photografting process of 240 s.

#### 41 **Figure 4**

#### 46 **Table 2**

51 As we have described before, the information provided by SEM analysis is and a  
52 complementary roughness study is useful to evaluate changes in topography due to the  
53 UV photografting process. In fact, the previous roughness study has revealed important  
54 changes in the micro-scale range. Nevertheless, due to the nature of the UV  
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1 photografting process, it is interesting to obtain qualitative and quantitative information  
2 about surface topography and this information can be obtained by using atomic force  
3 microscopy (AFM). Figure 5 shows 3D representation of surface topography (20x20  
4  $\mu\text{m}^2$ ) for untreated PP surface (Figure 5a) and PP surface with different exposure times  
5 to UV photografting process in the 60-240 s range. The information obtained by AFM is  
6 similar to that obtained with the roughness study but a nano-scale range due to the  
7 sensitiveness of AFM in this measurement range. The AFM 3D representation of the  
8 untreated sample (Figure 5a), is characterized by very smooth surface. The  $R_{\text{rms}}$  value  
9 for this surface is about 50 nm. We can observe that as the exposure time to UV  
10 photografting process increases, the overall roughness topography of PP surface also  
11 increases. For higher exposure times, around 240 seconds, the height difference between  
12 peaks and valleys is very pronounced.

### 31 **Figure 5**

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36 The three-dimensional topography representation of untreated PP is very smooth  
37 if compared to the topography of PP with different exposure times to UV photografting.  
38 We can also observe the influence of the exposure time to UV in the overall topography  
39 representation. The longer is the exposure time, the rougher is the topography of the  
40 treated polypropylene surface. Tab. 3 shows the values of root mean squared roughness  
41 values ( $R_{\text{rms}}$ ) and maximum of all micrographs analyzed.

### 53 **Table 3**

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Roughness values for 0-second exposure correspond to those in the untreated sample. The roughness values, both mean and maximum, show an upward trend with increasing exposure time. The  $R_{\text{rms}}$  roughness value for untreated polypropylene is about 26.59 nm, while PP surface with an exposure time of 240 s to UV photografting is close to 310.11 nm and this represents a remarkable increase in surface roughness. These results are in accordance with previous results obtained in the micro-scale roughness study and overall wetting changes.

#### 4. Conclusions.

UV photografting of methyl methacrylate (MMA) monomer is an efficient technique to improve the low intrinsic wetting properties of polypropylene substrates. The increase in wettability is evident from the observation of the evolution of contact angles with different test liquids. In accordance with this, the total free surface energy increases from 31.5  $\text{mJ m}^{-2}$  for untreated polypropylene up to values around 57.5  $\text{mJ m}^{-2}$  for polypropylene substrates with an exposure time to UV photografting of 240 s. It is important to remark that substantial changes are detected in the polar component of the total surface free energy which changes from 3.0  $\text{mJ m}^{-2}$  for untreated polypropylene up to 26  $\text{mJ m}^{-2}$  for exposure times in the 210-240 s range. The FTIR study has revealed presence of polar groups derived methyl methacrylate monomers which have been chemically bonded in the top most layers of polypropylene substrates and this is responsible for an increase in surface functionalization. On other hand, the SEM analysis has revealed qualitative changes in surface topography as the exposure time to UV photografting process increases. These changes have been quantified at a micro- and a nano-scale range by using conventional roughness study and AFM respectively. In both cases, a marked increasing tendency of average roughness values is obtained



1 thus indicating that the improvement of polypropylene wetting properties is achieved by  
2 functionalization and changes in surface topography.  
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## 6 **Acknowledgements**

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**Table captions**

**Table 1.-** Variation of total surface free energy ( $\gamma_s$ ) and its polar ( $\gamma_s^p$ ) and dispersive ( $\gamma_s^d$ ) contribution of polypropylene surface in terms of the exposure time to methyl methacrylate UV photografting.

**Table 2.-** Variation of average roughness (Ra) and height of average roughness (Rz) in terms of the exposure time to methyl methacrylate UV photografting.

**Table 3.-** Variation of root mean squared roughness (Rrms) and max Z heigh obtained by AFM analysis in terms of the exposure time to methyl methacrylate UV photografting.

## Figure legends

**Scheme 1.-** Formation of free radicals on benzophenone photoinitiator by UV radiation followed by hydrogen abstraction on polymer chain.

**Scheme 2.-** Reaction of free radicals derived from photoinitiator and polymer chain with acrylic monomer by addition processes.

**Scheme 3.-** Termination stage of the photopolymerization process of polymer substrate in presence of photoinitiator and acrylic monomer.

**Figure 1.-** Evolution of the static contact angle in terms of the exposure time to methyl methacrylate UV photografting for different test liquids.

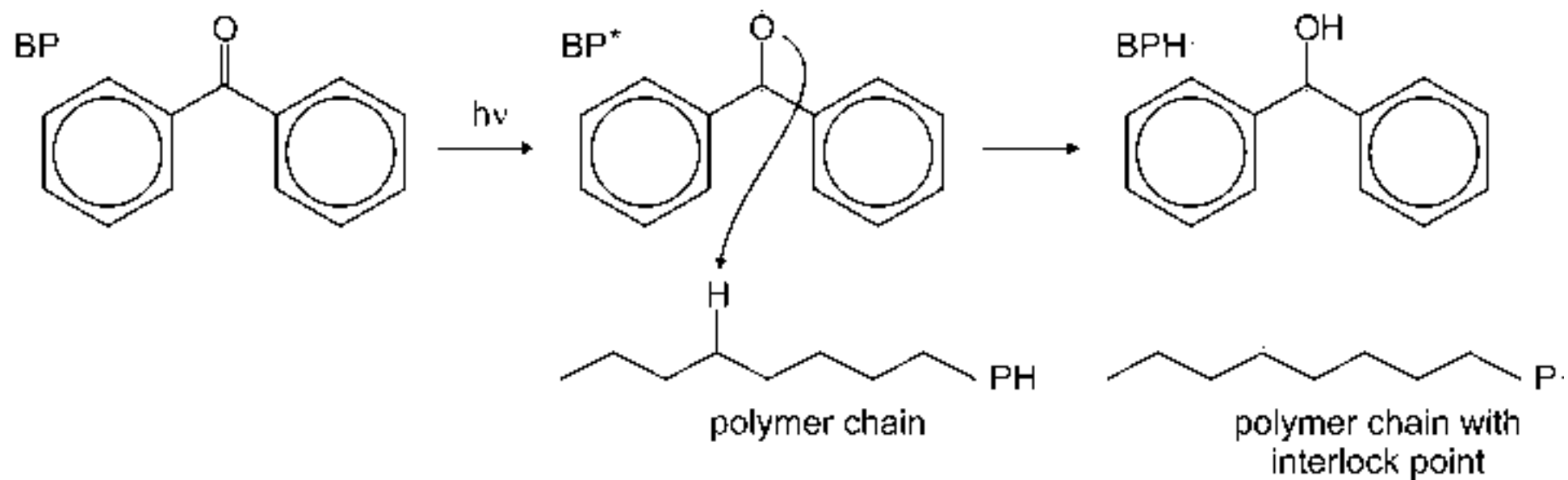
**Figure 2.-** FTIR-ATR spectra of polypropylene surface with different exposure times to methyl methacrylate UV photografting.

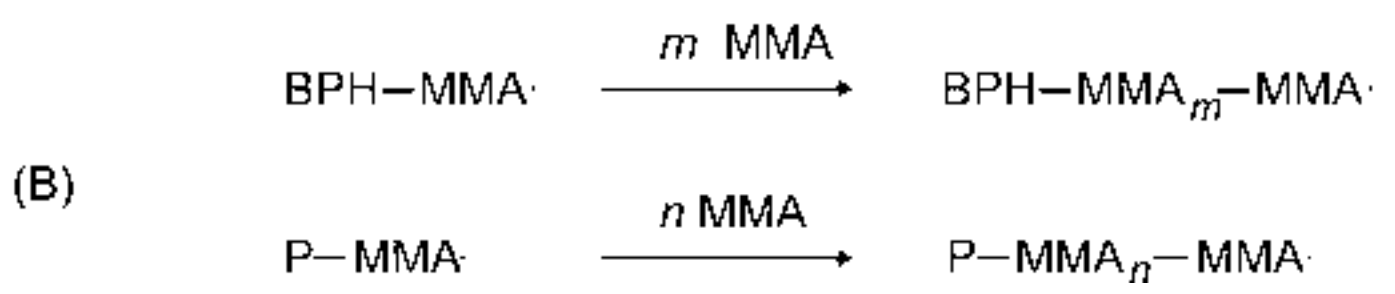
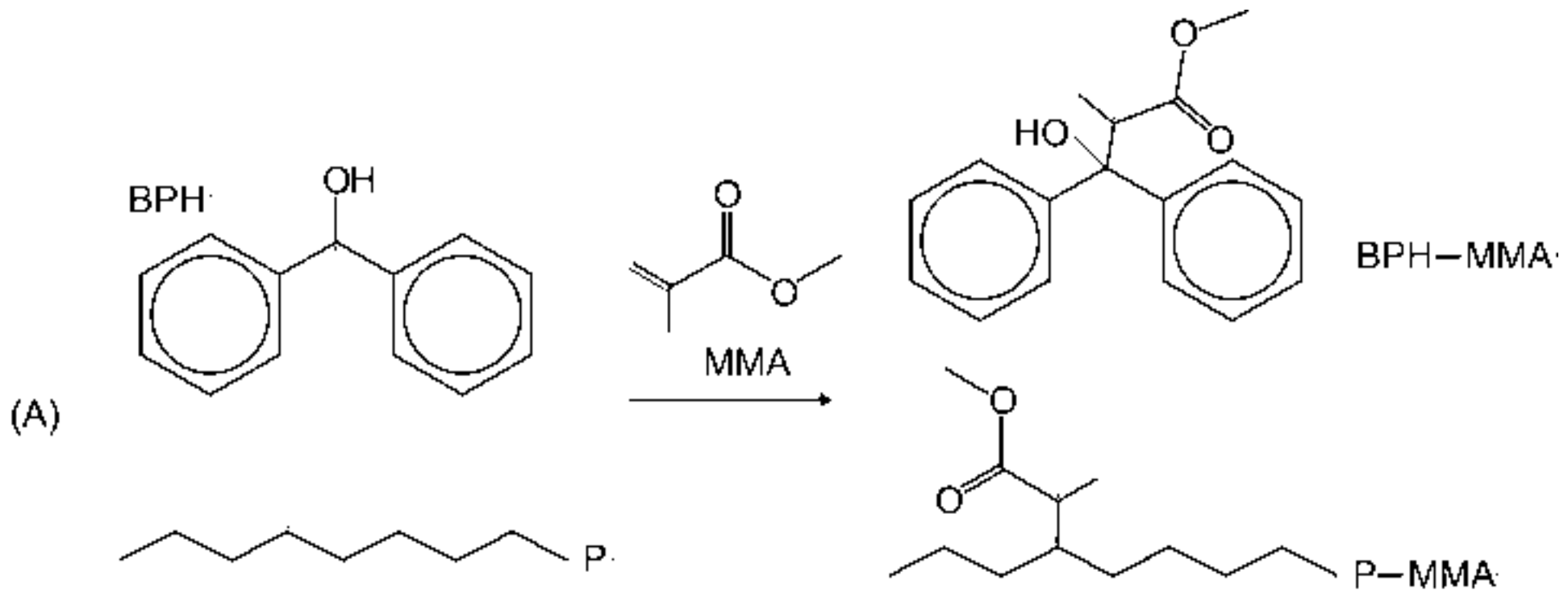
**Figure 3.-** SEM microphotographs (400x) and corresponding water contact angle photos for different exposure times to methyl methacrylate UV photografting, a) 0 s, b) 60 s, c) 120 s and d) 180 s.

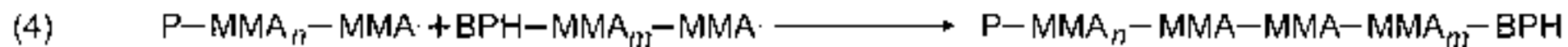
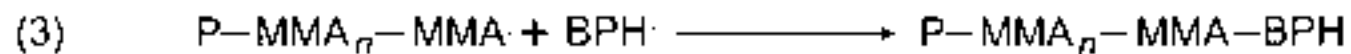
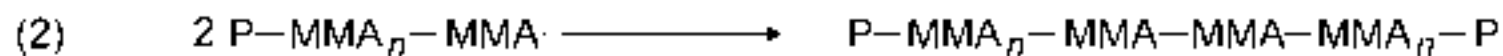
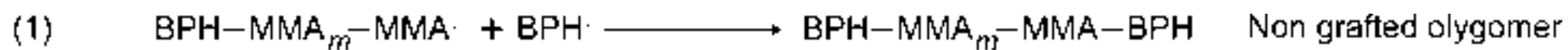
**Figure 4.-** Comparative plot of the roughness profiles of polypropylene surfaces with different exposure times to methyl methacrylate UV photografting.

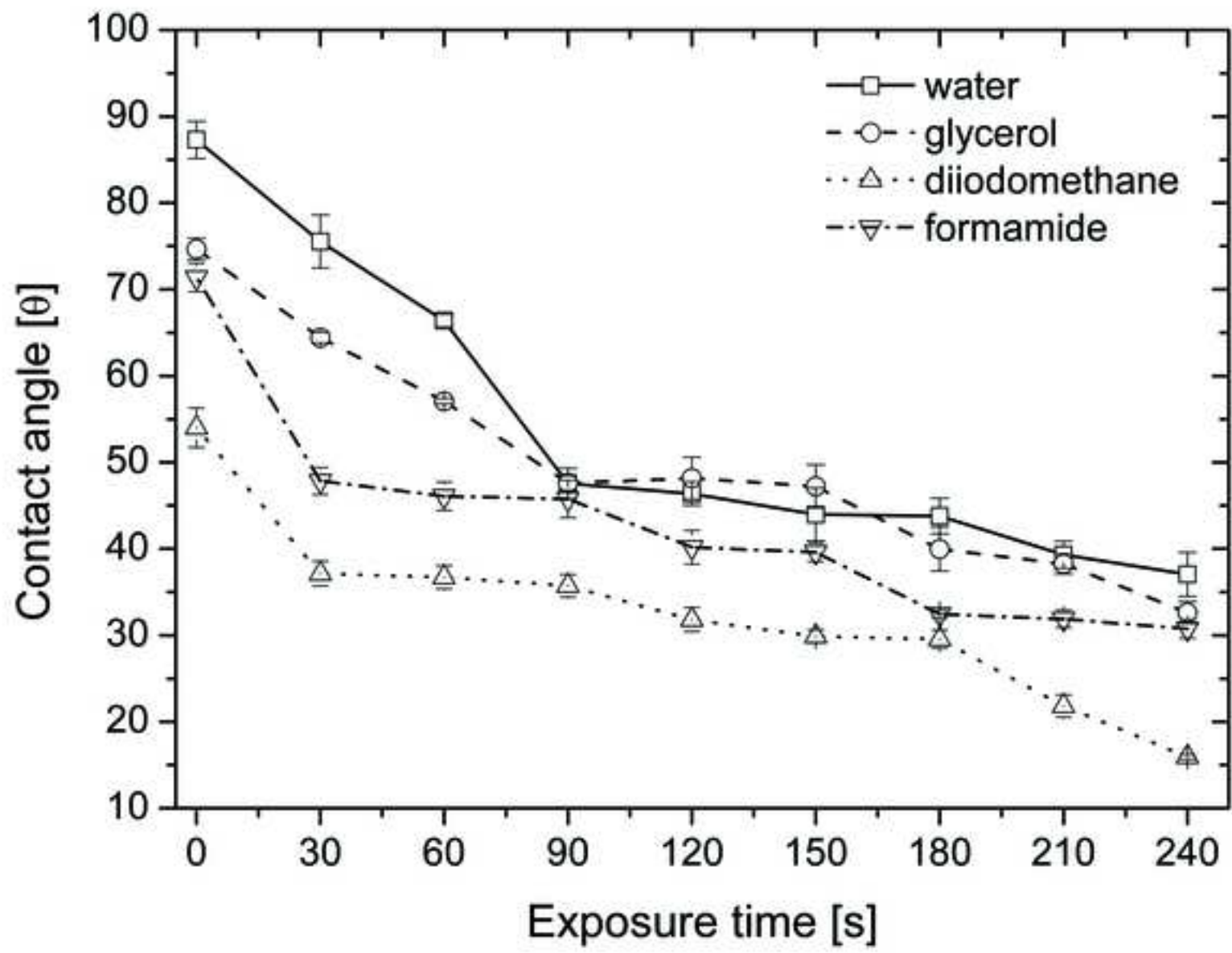
**Figure 5.-** Topographic 3D-AFM graphs of polypropylene surface with different exposure times to methyl methacrylate UV photografting.

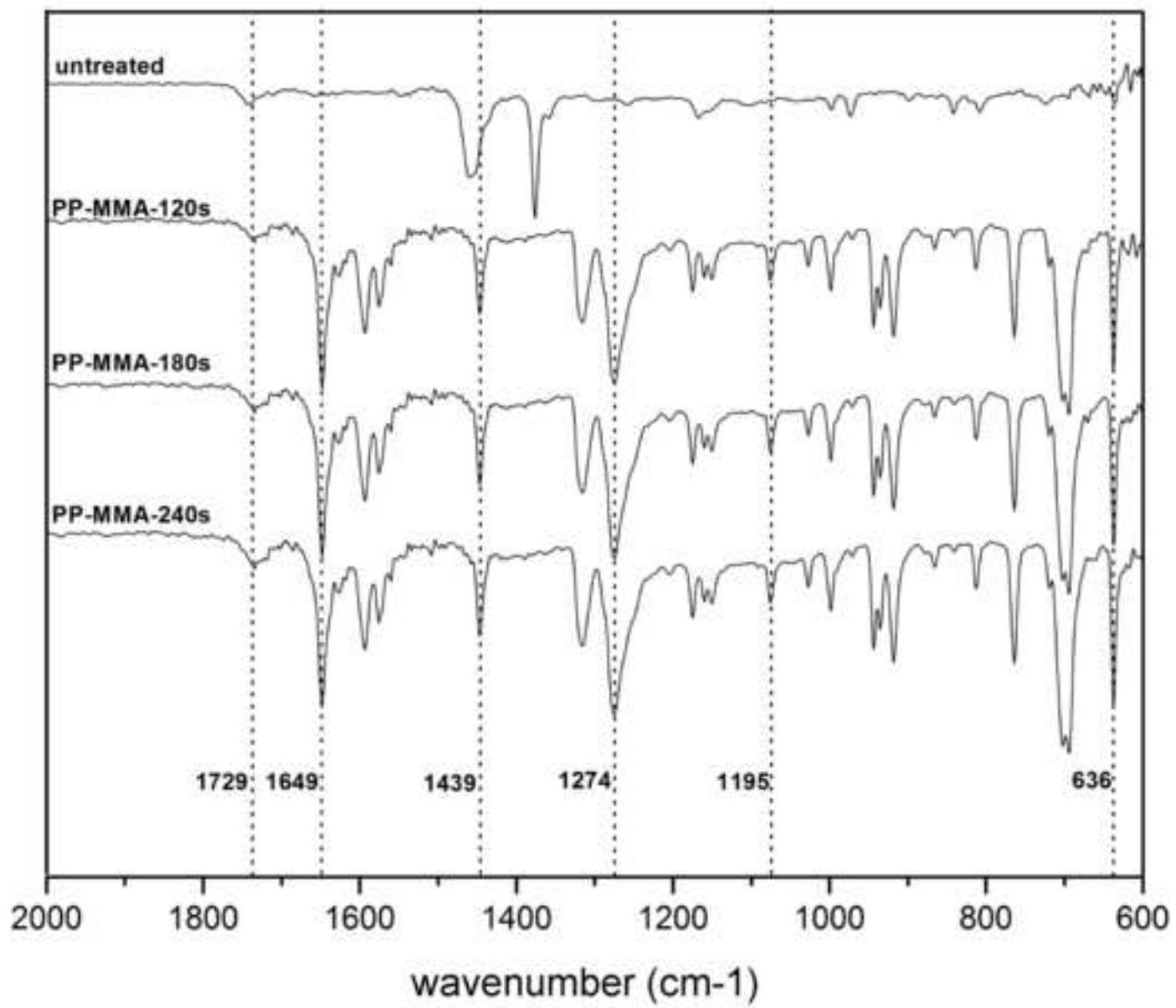


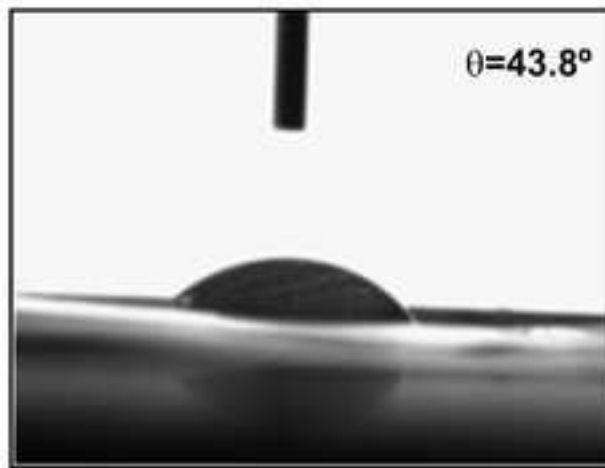
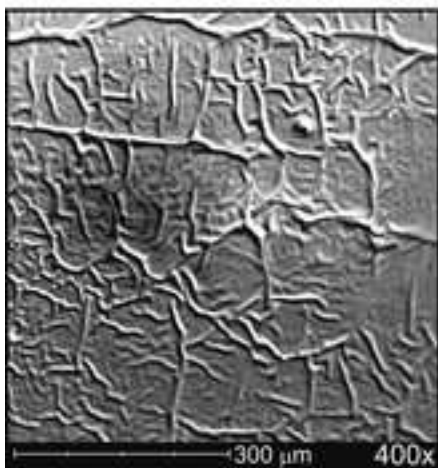
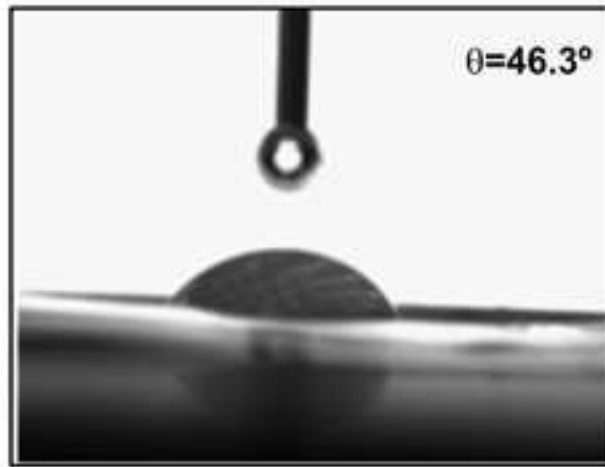
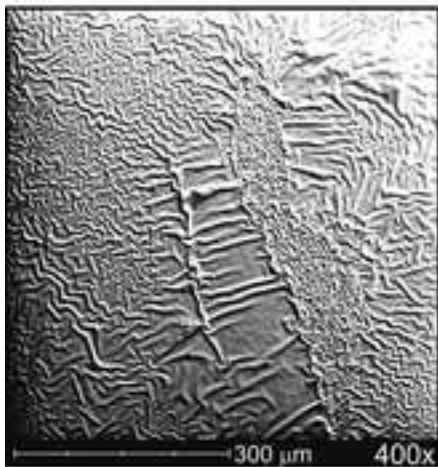
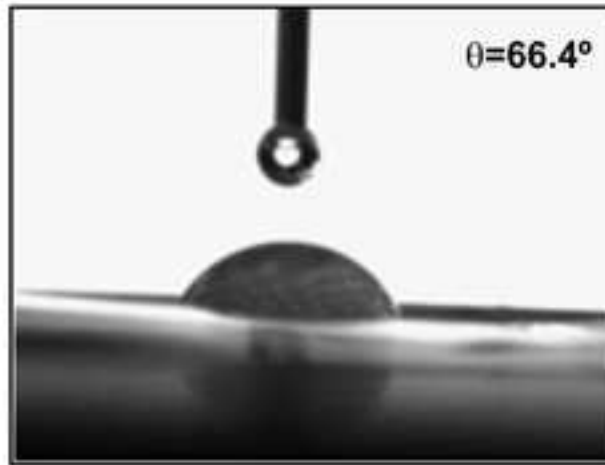
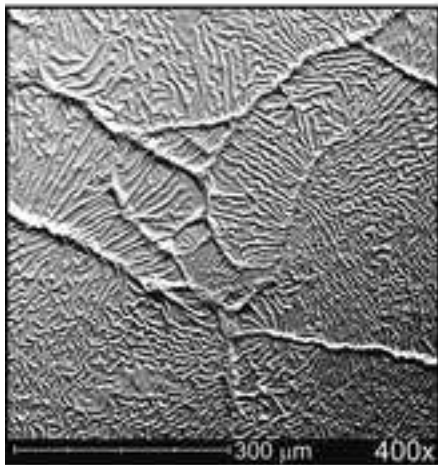
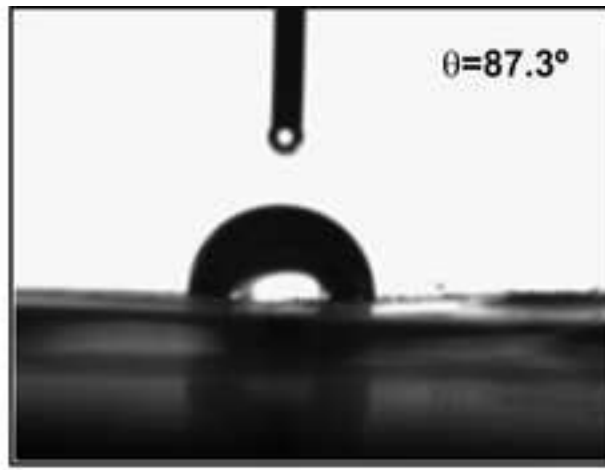
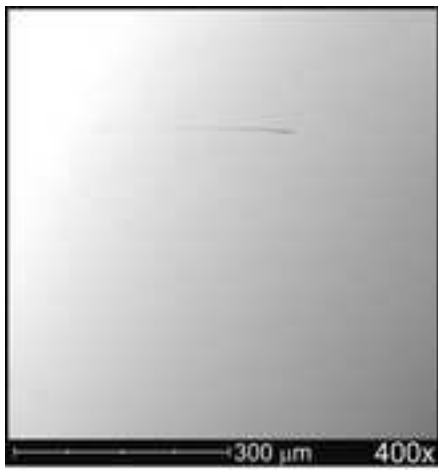


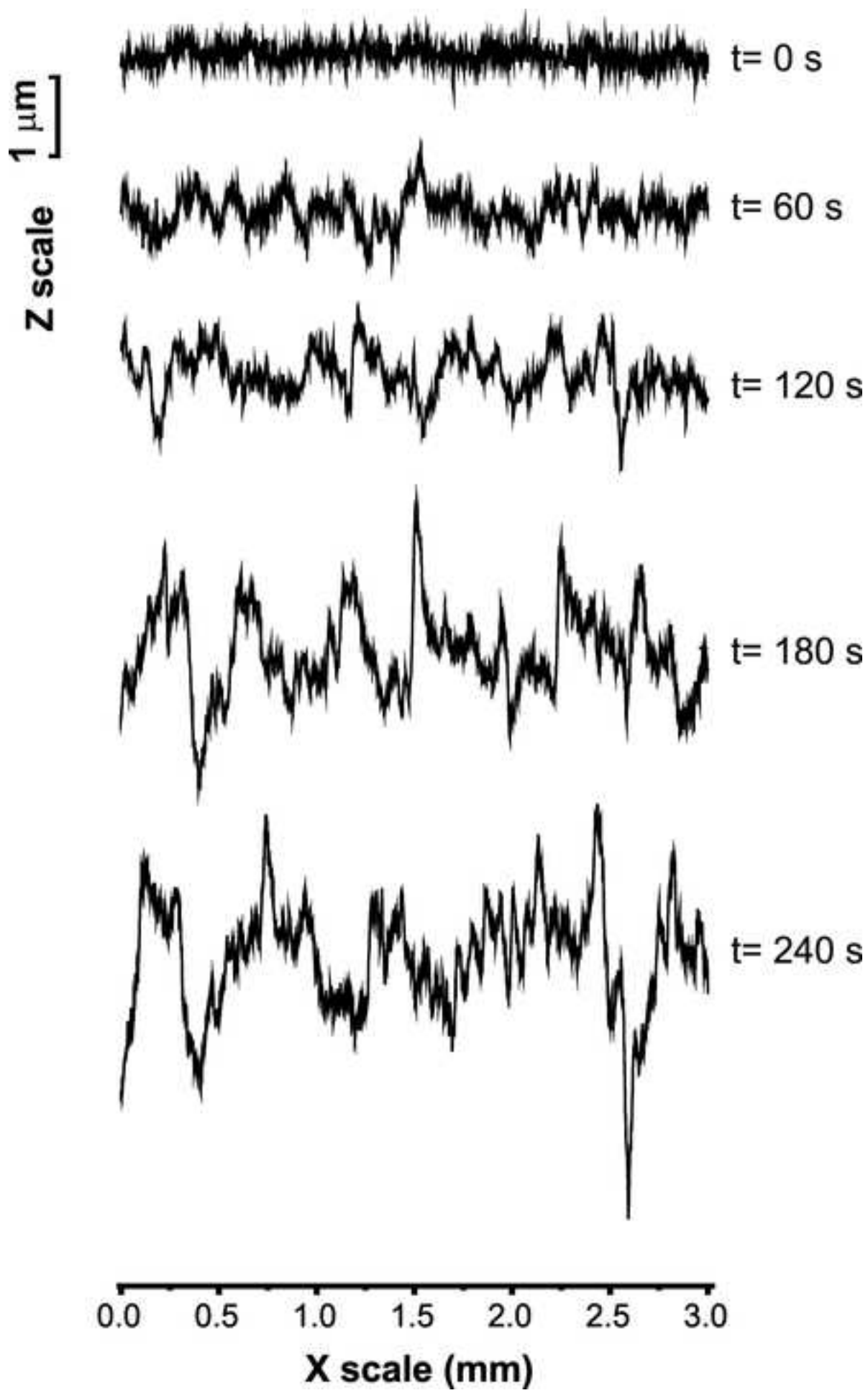


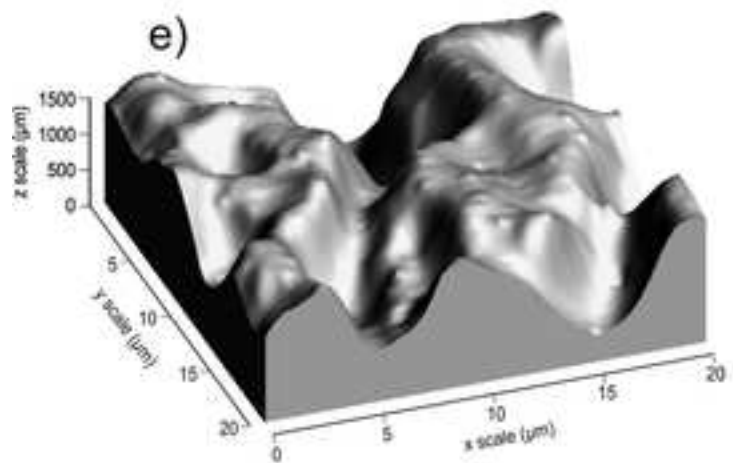
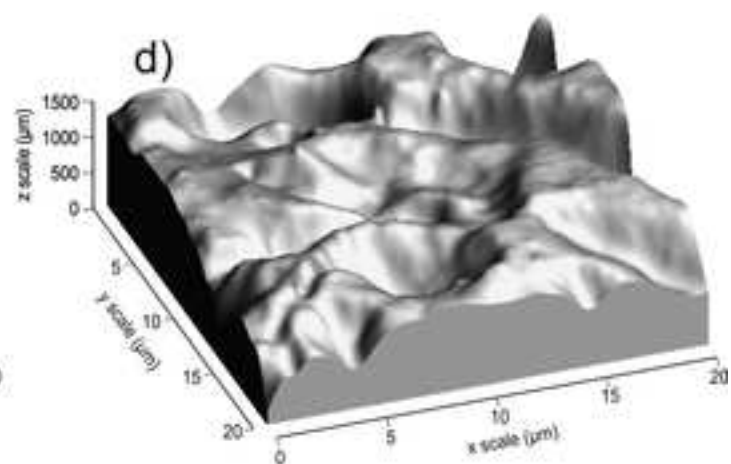
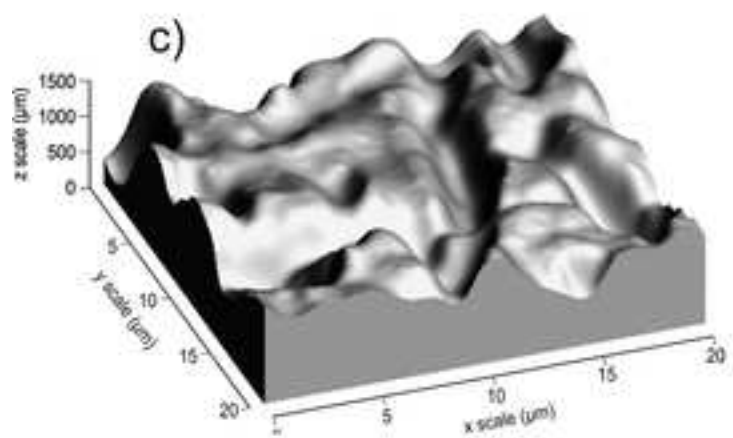
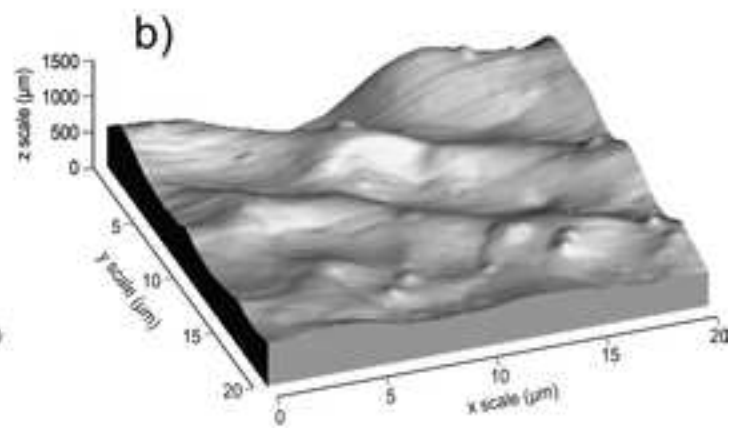
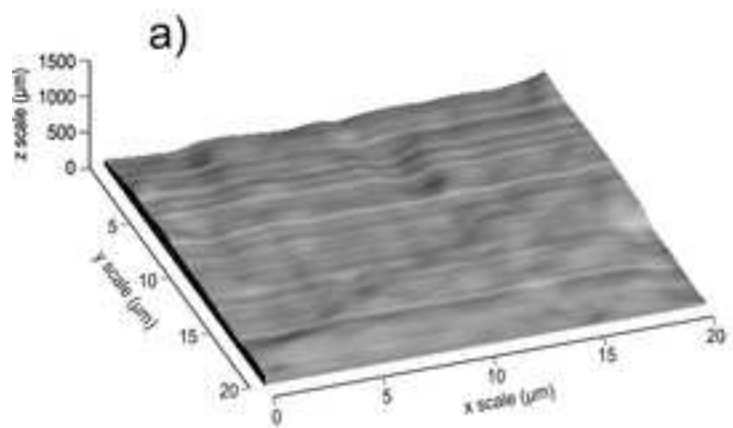














**Table 1.-**

<b>Exposure time [s]</b>	<b><math>\gamma_s</math> [mJ m<sup>-2</sup>]</b>	<b><math>\gamma_s^p</math> [mJ m<sup>-2</sup>]</b>	<b><math>\gamma_s^d</math> [mJ m<sup>-2</sup>]</b>
0	31.4	3.0	28.4
30	42.2	5.5	36.6
60	43.4	10.4	33.0
90	48.7	23.0	25.7
120	49.9	22.2	27.7
150	51.2	23.9	27.2
180	53.6	24.3	29.3
210	55.6	25.6	30.0
240	57.5	26.2	31.3

**Table 2.-**

<b>Exposure time [s]</b>	<b>Ra [<math>\mu\text{m}</math>]</b>	<b>Rz [<math>\mu\text{m}</math>]</b>
0	0.11	0.89
60	0.17	1.37
120	0.31	2.98
180	0.41	2.63
240	0.53	3.36

**Table 3.-**

<b>Exposure time [s]</b>	<b>Rms [nm]</b>	<b>Rmax [nm]</b>
0	26.6	155.0
60	99.3	669.6
120	179.1	1150.0
180	265.9	1380.1
240	310.1	1409.1