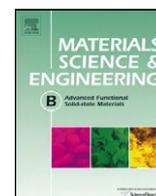




Contents lists available at [ScienceDirect](http://www.sciencedirect.com)

## Materials Science and Engineering B

journal homepage: [www.elsevier.com/locate/mseb](http://www.elsevier.com/locate/mseb)



# Correlations between the structure and the morphology of PET–rubber nanocomposites with different additives

C. Vladuta\*, M. Voinea, E. Purghel, A. Duta

Transilvania University of Braşov, Centre: Product Design for Sustainable Development, Eroilor 29, 500036 Braşov, Romania

### ARTICLE INFO

#### Article history:

Received 29 August 2008  
Received in revised form 18 February 2009  
Accepted 7 July 2009

#### Keywords:

PET–rubber nanocomposites  
HDPE  
LDPE  
TiO<sub>2</sub> nanoparticle  
Surface and interface states  
Contact angle

### ABSTRACT

The influence of different additives: high density polyethylene (HDPE), low density polyethylene (LDPE) and TiO<sub>2</sub> nanoparticles on the polyethylene terephthalate (PET)–rubber nanocomposite interface was investigated. The composites obtained by compression moulding from tire rubber and PET bottles' waste were partially heterogeneous and partially compatible, as confirmed by the FTIR measurements. The type of additives and the curing temperature proved to have a strong effect on the interface(s) and surface properties due to the different inter- and intra-molecular bonds between the composites' constituents. The use of HDPE leads to the largest interfacial change, while the samples with LDPE have a higher degree of porosity/roughness. The composites with TiO<sub>2</sub> present a more compact polymer surfaces and higher contact angle value with water, at the initial moment. Titania nanoparticles can be used, thus, as a tool for tailoring the composite wettability. By choosing the adequate additive(s), PET–rubber can be compatibilized to obtain good interfacial adhesion and to reduce the interfacial tension between the components.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

Recycled polymer materials have been widely used in various industrial applications because of their superior properties. The main problems in their recycling rise from their degradation during processing and the incompatibility between polymers [1].

Thermodynamic immiscibility of most polymers is a serious barrier in mixtures processing of both virgin polymer and plastic waste [2]. As a consequence, adhesion between individual molecules of materials made from these polymer blends is too low. In many cases, too low mechanical strength of these materials is an unfavorable result. In order to enhance the material strength, small amounts of additives are being added to the polymer mixtures. Therefore compatibilization, in order to obtain good interfacial adhesion and to reduce the interfacial tension between the components, is necessary. The interfacial adhesion [3] of individual components of the blends is improved.

However, the use of additives is sometimes limited due to the surface characteristics. It is, therefore, interesting to modify the surface in a controlled manner to enhance wettability, adhesion and compatibility with other materials. The most important feature of the surface modification is that the surface properties of the

treated material can be modified without changing their intrinsic bulk properties [4].

In this paper, the effect of high density polyethylene (HDPE), low density polyethylene (LDPE) and TiO<sub>2</sub> nanoparticles on the PET–rubber nanocomposites have been analyzed and correlated with the surface properties with influence on the compatibility.

## 2. Experimental

### 2.1. Materials

Waste materials were used from tire rubber, HDPE and PET bottles, and LDPE from plastic bags. These were washed and milled in particles with 1 mm dimension. Commercially available TiO<sub>2</sub> (Degussa P25) with a mean primary size of 21 nm and a specific surface area of 50 m<sup>2</sup>/g was used. The nanoparticles consist of approximately 80% anatase and 20% rutile.

### 2.2. Techniques

To prepare composites by compression moulding, a manual press was used and set to 220, 240 and 260 °C. Moulding time was 1 h, using a thermostatic heater and there were obtained samples with similar composition of the main constituents (tire rubber and PET), but with different additives (HDPE, LDPE, TiO<sub>2</sub>, 5 wt%).

\* Corresponding author. Tel.: +40 721 087 089; fax: +40 268 475597.  
E-mail address: [c.vladuta@unitbv.ro](mailto:c.vladuta@unitbv.ro) (C. Vladuta).

### 2.3. Analysis

#### 2.3.1. Fourier Transform Infrared Spectroscopy (FTIR) analysis

Fourier Transform Infrared Spectroscopy (FTIR) analysis using a spectrophotometer (Spectrum BX Perkin Elmer) was used to record spectra in reflectance mode, in the range from 500 to 4500  $\text{cm}^{-1}$ , after 4 scans, with resolution of 4  $\text{cm}^{-1}$ . The chemical structure of the plastics, tire rubber waste and composites, before and after the recycling technique was confirmed by recording their IR spectra.

#### 2.3.2. Differential scanning calorimetry analysis

Thermal characterization of the composites was carried out by differential scanning calorimetry, DSC (PerkinElmer, DSC-2). The thermal parameters, melting temperature ( $T_m$ ), and melting enthalpy ( $\Delta H_m$ ), were calculated. The experiments were done in inert atmosphere ( $\text{N}_2$ ) from  $-100$  to  $300^\circ\text{C}$  in an aluminum pan with a heating rate of  $10^\circ\text{C}/\text{min}$ .

#### 2.3.3. Contact angle measurement

An OCA-20 Contact Angle System (DataPhysics Instruments) was used to determine contact angle of the composites surface. A drop of distilled water ( $10\ \mu\text{L}$ ) was placed, with  $1\ \mu\text{L}/\text{s}$  velocity, on the composites surface, and the contact angle was measured every second during 30 min.

Surface energies were estimated using the theory of the adhesion work among solid and liquid phases, where polar and non-polar (dispersive) contributions in the interaction processes

are considered, using ultra pure water (Direct-Q 3 Water Purification System)—which is the highly polar liquid with  $\sigma = 72.10\ \text{mN}/\text{m}$  ( $\sigma^p = 52.20\ \text{mN}/\text{m}$ ;  $\sigma^d = 19.90\ \text{mN}/\text{m}$ ) [5].

#### 2.3.4. X-ray analysis

The X-ray diffraction measurements, Bruker D8 advance Diffractometer Cu  $K\alpha$  radiation of  $\lambda = 1.54016\ \text{\AA}$ , were used to evaluate the effect of HDPE, LDPE and  $\text{TiO}_2$  nanoparticles on the interfaces and composites crystalline structure. Data were collected over the range  $2\theta = 5\text{--}60^\circ$  in the fixed time mode with a step interval of  $0.01^\circ$  at  $25^\circ\text{C}$  temperature.

#### 2.3.5. Atomic force microscopy

The surface morphology of the nanocomposite surface was investigated by atomic force microscopy (AFM NT-MDT model NTE-GRA PRIMA EC). The images were taken in semi-contact mode with "GOLDEN" silicon cantilever (NCSG10, force constant  $0.15\ \text{N}/\text{m}$ , tip radius  $10\ \text{nm}$ ).

## 3. Results and discussions

### 3.1. Fourier Transform Infrared Spectroscopy (FTIR) analysis

The FTIR spectra of the composite with HDPE, LDPE and  $\text{TiO}_2$  are discussed compared with the second raw material spectra [6]. Displacement can be observed in the reflectance maxima due to vibration alterations of the dipoles existing in the polymers caused

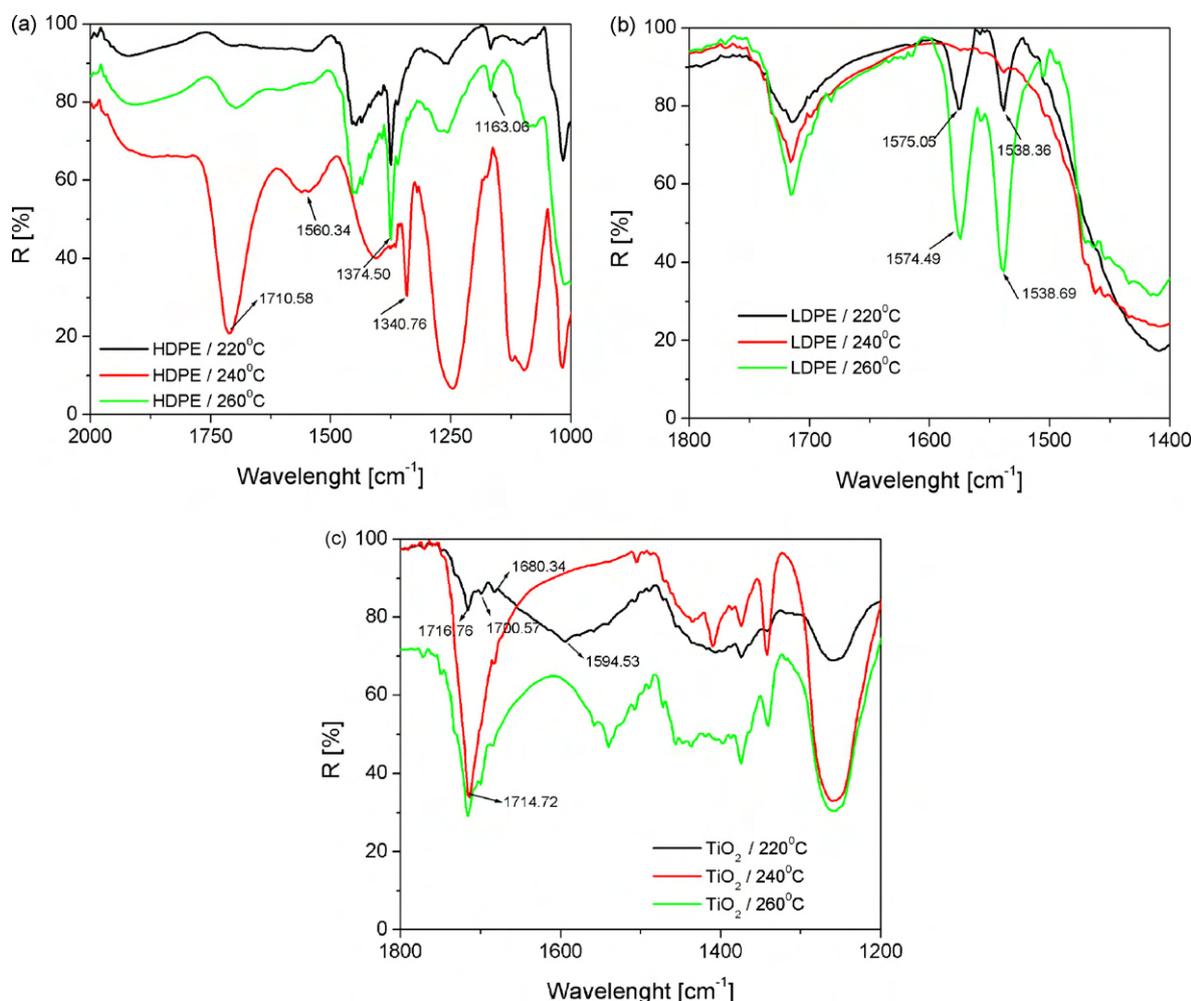


Fig. 1. FTIR spectra for the composites with: (a) HDPE; (b) LDPE; (c)  $\text{TiO}_2$ .

by the presence of additives. The type of additives and the curing temperature can affect the inter- and intra-molecular bonds in the composites' constituents and at the interface(s). High polarity differences lead to peak modification towards higher wavelengths values; while for small polarity differences the shift is towards higher values of the wave number ( $\text{cm}^{-1}$ ), showing different interaction mechanisms.

The characteristic bands corresponding to the samples with HDPE obtained at  $220^\circ\text{C}$  are those at  $960.24$  and  $900.15\text{ cm}^{-1}$ , the vinyl groups ( $-\text{CH}=\text{CH}_2$ ). These peaks join for the samples obtained at  $240^\circ\text{C}$ , but the peak at  $960.24\text{ cm}^{-1}$  absconds in the samples obtained at  $260^\circ\text{C}$ , because of the oxidation favored by the higher temperature. New peaks are formed in the sample at  $240^\circ\text{C}$  ( $3412.08$ ,  $1710.58$ ,  $1560.34\text{ cm}^{-1}$ ) that can be assigned to interface interactions between the tire rubber matrix, PET and HDPE (Fig. 1a). In the samples with LDPE obtained at  $240^\circ\text{C}$ , new peaks are formed ( $670.80\text{ cm}^{-1}$ ) and the peaks  $1575.05$ ,  $1538.36\text{ cm}^{-1}$  disappear (Fig. 1b). Only one peak ( $1937.89\text{ cm}^{-1}$ ) is formed for sample obtained at  $260^\circ\text{C}$ . The peaks can be assigned to polar compounds, resulted via partial oxidation that can cause electrostatic interactions, stabilizing the interface.

Comparing the main peaks position in the nanocomposite ( $220$ ,  $240$ ,  $260^\circ\text{C}$ ) with the values known from the literature, it can be considered that  $\text{TiO}_2$  nanoparticles reduce the mobility of the saturated and aromatic sequences as a result of the interlamellar infiltration. These effects were higher at the lowest molding temperature ( $240^\circ\text{C}$ ). The physical and chemical interactions between  $\text{TiO}_2$  nanoparticles with PET and tire rubber powder have been

confirmed by new peaks ( $1342.10$ ,  $871.49$ ,  $790.14\text{ cm}^{-1}$ ). The peak at  $1594.53\text{ cm}^{-1}$  disappears and three peaks ( $1716.76$ ,  $1700.57$ ,  $1680.34\text{ cm}^{-1}$ ) may overlap and they can be associated to one single reference peak at  $1714.72\text{ cm}^{-1}$  (Fig. 1c). The peak shift is constant for the composites with  $\text{TiO}_2$  nanoparticle obtained at  $220$ ,  $260^\circ\text{C}$ , proving that the structural modifications by interfacial bonding follow the same mechanism.

A shift to lower wave numbers (lower energies) is registered for the  $-\text{CH}_2-$ ,  $-\text{CH}_3$  groups and aromatic rings, proving more disordered arrangements in the nanocomposite. At the same time, the shift towards higher energy of the double bonds can be responsible for the short-range ordering, that can result in new crystallite formation. This is obviously linked to the interaction with  $\text{TiO}_2$ , for which the  $\text{Ti}-\text{O}$  bond acts in structural reinforcement. The samples obtained at  $240^\circ\text{C}$  seem to have better interface properties, as a consequence of physical and chemical interactions.

Based on the spectra modifications we can conclude that the largest interfacial change result when using HDPE.

### 3.2. Contact angle measurements

The contact angle is a surface property, a consequence of intermolecular interactions. Contact angle is strongly dependent on the liquid and surface nature, solid/liquid contact time and surface charge of composites. The liquid adsorption/absorption appears to start as soon as solid and liquid come in contact, i.e. in a fraction of a second. Water adsorption on the composite and water penetration into the solid were suggested as the plausible mechanisms

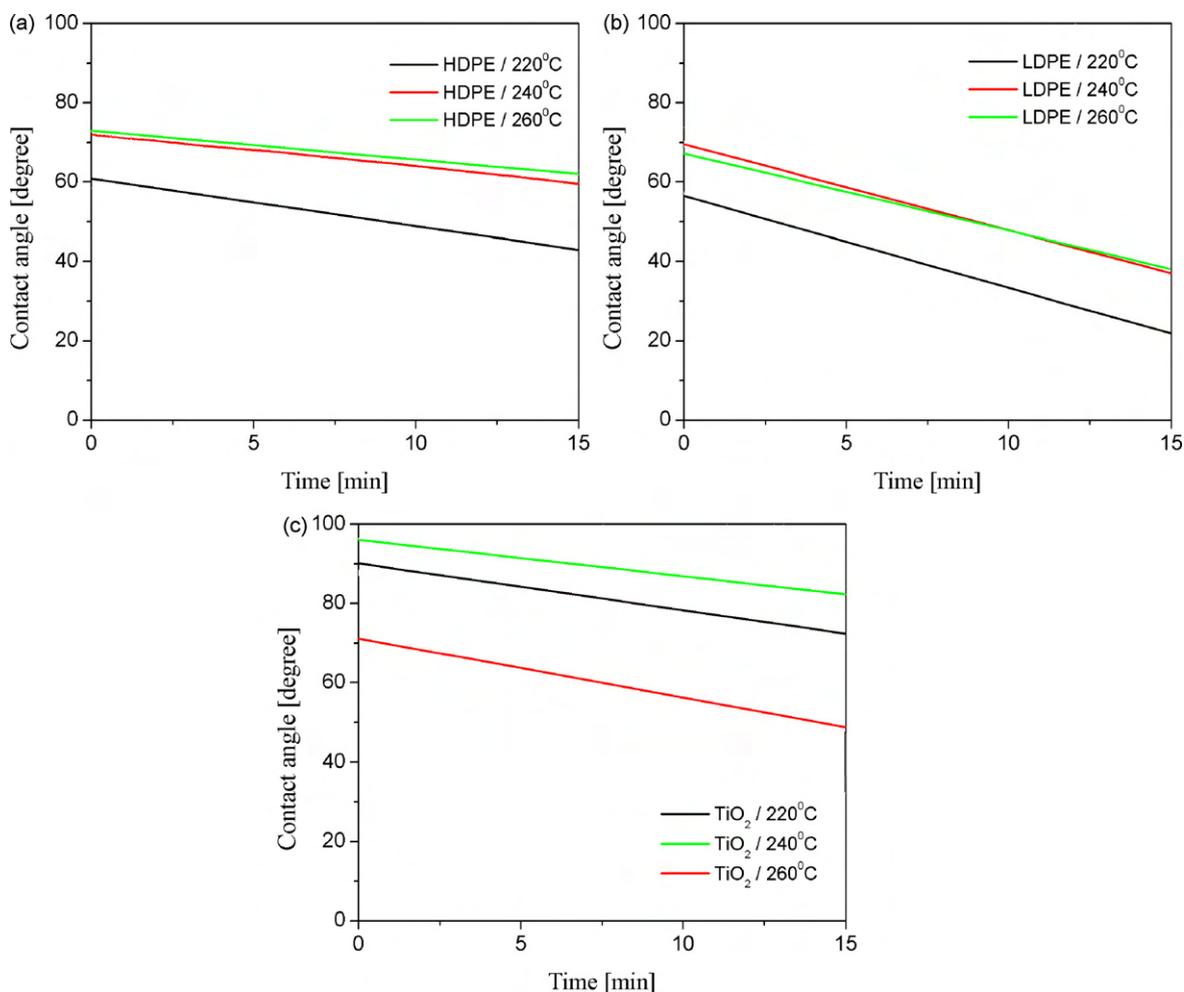


Fig. 2. Contact angle time dependence for the samples with: (a) HDPE; (b) LDPE; (c)  $\text{TiO}_2$ .

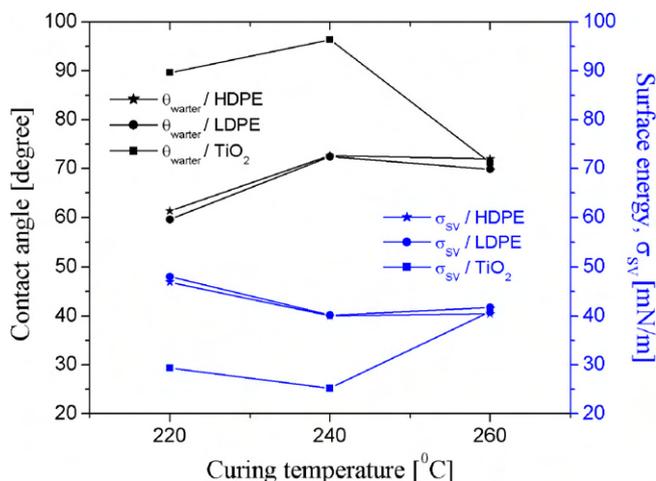


Fig. 3. The contact angle values at initial moment and the values of the solid surface energy.

that cause the angles to decrease with the solid–liquid contact time (Fig. 2a–c). Consequently, the solid–liquid interfacial tension ( $\sigma_{SL}$ ) is decreases over time.

The absence of polar functional groups able to form hydrogen bonds with water molecules and the high packing density of the macromolecules on the supermolecular level (with marked ordering even in quasi-amorphous regions) create steric and kinetic hindrances for penetration of low-molecular-weight molecules in composite. This results in low energy of the surface reaction with water and the reduced capacity of composite to absorb low-molecular-weight substances, primarily moisture, which is a highly desirable property for further applications.

The larger slopes for composites with HDPE are presumably due to more extensive liquid sorption/penetration. They show lower adsorption rate than the composites with LDPE confirming that the latest have the most opened structure, as also the mechanical properties suggested. The data show that TiO<sub>2</sub> induces stronger surface modifications than HDPE and LDPE, confirmed by the higher value of the contact angle for water on TiO<sub>2</sub> substrate (96.39° for sample obtained at 240 °C), measured at the initial contact moment.

The  $\theta$  values recorded at the initial moment of the drop–composite contact are presented (Fig. 3). In all cases contact angles below 90° were recorded but these values, on a horizontal surface, vary with the substrates nature and porosity. The slopes of  $\theta$  as a function of time may be correlated with the adsorption and/or absorption rate of the liquid on/in the composites. This depends on the composite morphology and on the solid–liquid interaction energy. This surface energy is presented (Fig. 3). The surface energy depends on the chemical structure of the solid, nature of filler. The lower surface energy values (in the case of composites with TiO<sub>2</sub>) can be correlated with the formation of more compact polymer surfaces and represents a tool in tailoring the composite wettability.

The conclusion can be that the samples with LDPE have a higher degree of porosity/roughness. These results will be further correlated with AFM data. For all the composite types obtained at 240 °C, the lowest water wettability was recorded and this can be correlated with the stronger interface bonds, as proved by FTIR.

### 3.3. Differential scanning calorimetry (DSC) analysis

The values of the thermophysical parameters ( $T_m$ ,  $\Delta H_m$ ) obtained by the heating DSC thermograms for the samples with different fillers obtained at 240 °C are presented (Table 1). The thermal behaviors of the composites during the heating process are compared with those of the components (Table 2).

Table 1  
The thermophysical parameters of the composites.

Thermophysical properties	Composite with		
	HDPE	LDPE	TiO <sub>2</sub>
Melting temperature, $T_m$ [°C]	152.39	103.08	244.83
	229.73	244.73	
Melting heat, $\Delta H_m$ [J/g]	2.5603	4.9335	1.48

Table 2  
The thermophysical parameters for the recycled material.

Recycled material	$T_m$ [°C]	$\Delta H_m$ [J/g]
PET	248.83	40.64
Rubber	22.93	0.90
LDPE	121.81	0.32
HDPE	161.81	0.62

The DSC thermograms of the composite with LDPE and HDPE show two  $T_m$  values indicating a two-phase system. The first melting temperature can be assigned to  $T_m$  for HDPE (152.39 °C) and LDPE (103.08 °C), while the second melting temperature is the  $T_m$  for PET. During processing, tire rubber is in the molten phase and the result is the development of a rather weak interface between matrix, PET and filler.

The mixtures are partially compatible, indicating the physical bonds, thus confirming the assumptions based on the FTIR measurements.

### 3.4. X-ray analysis

In a polymer compound, the contribution from small crystals in the X-ray spectra is lost in the amorphous halo. The amorphous regions yield to a broad halo, partially overlapping the strong and sharp diffraction pattern of the crystallites. The XRD measurements show changes in crystallinity for the composites with different additives. All diffraction patterns for the samples obtained at 240 °C are presented (Fig. 4).

The lower crystallinity value from the XRD of the PET–rubber nanocomposites/TiO<sub>2</sub> nanoparticles was consistent with the formation of poorly organized crystals in this sample. Considering also the FTIR results, we can conclude that the main influence in the composite behavior is due to the –CH<sub>2</sub>– and –CH<sub>3</sub> bonds and the aromatic rings.

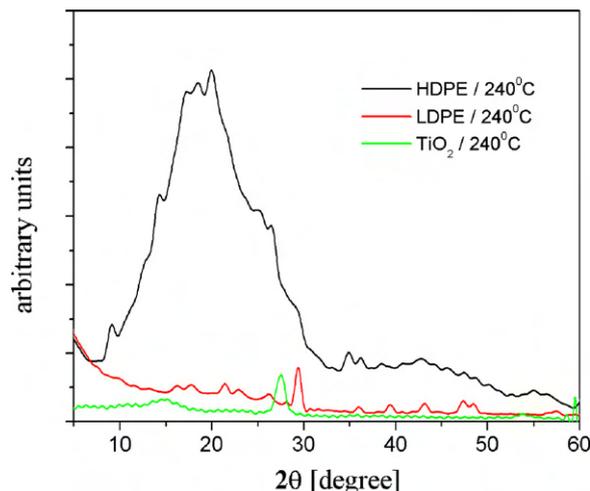


Fig. 4. The XRD patterns for the composites with HDPE, LDPE and TiO<sub>2</sub>.

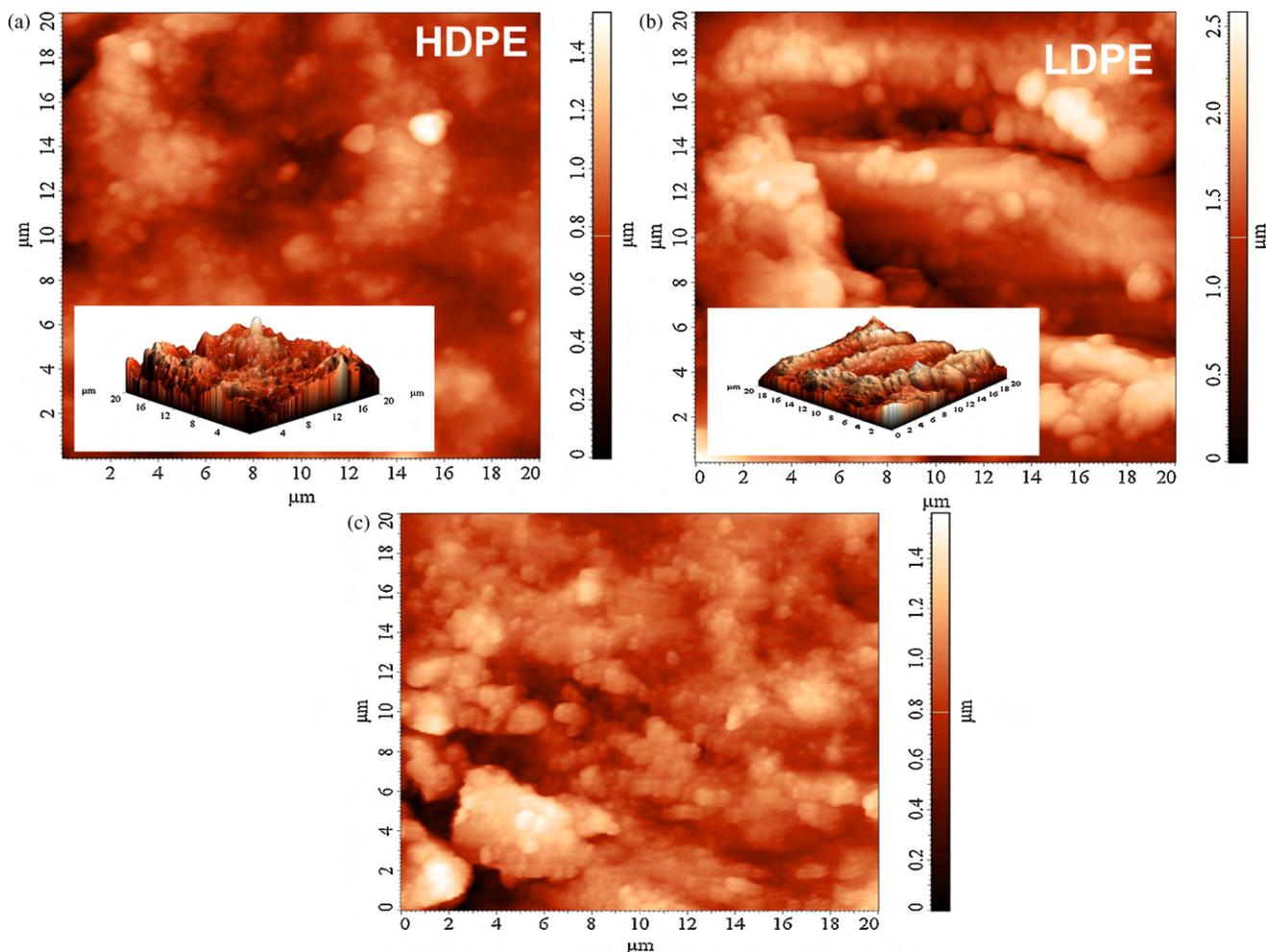


Fig. 5. AFM micrograph for the samples with: (a) HDPE; (b) LDPE; (c) TiO<sub>2</sub>.

A higher crystallinity degree can be the result of (re)arrangement in the polymer(s) and/or phase transitions (amorphous–crystalline), such as in case of the composites with HDPE. Thus, based on the FTIR and XRD results we can conclude that physical and/or chemical interactions took place for the composites obtained at 240 °C.

### 3.5. Atomic force microscopy (AFM)

The AFM analysis of the surfaces showed modified morphologies for the samples with different fillers. All composites were relatively smooth and homogenous (Fig. 5a–c). The surface RMS of the composites can be correlated with the water contact angle and the results show that composites with high roughness (large, open pores) correspond to low contact angles; the observation is valid both for porous HDPE and LDPE.

A more homogeneous surface is likely to be obtained for the sample obtained at 240 °C with HDPE (RMS=360 nm), compared with the samples with LDPE (RMS=535 nm) and TiO<sub>2</sub> (RMS=427 nm).

The roughness values suggest an increase in the surface tortuosity when using LDPE and TiO<sub>2</sub>, implying that surface morphology variations are likely to involve also molecular entanglement/crosslinking. The higher roughness is mainly the result of the C=C bonds oxidation that can also form volatile compounds, leaving large pores in the surface.

## 4. Conclusions

The effect of the HDPE, LDPE and TiO<sub>2</sub> nanoparticles on the PET–rubber interface in nanocomposites was investigated based on the physical–chemical interactions. The modifications in surface energy, morphology and crystalline structure were discussed.

The FTIR spectra obtained from nanocomposites with different additives, show differences. Displacement of the reflectance maxima of the bands can be observed, because the dipoles in the polymers undergo vibration alterations due to the changes caused by the additives in intermolecular interactions. New peaks confirm the (interfacial) chemical reactions, mainly oxidation.

In good agreement with the FTIR analysis, the DSC curves of the mixed composites' constituents contain two melting peaks, that is, the mixtures are partially heterogeneous and partially compatible. The addition of TiO<sub>2</sub> nanoparticles results in the decrease of the crystallinity degree and in the increase of the surface roughness.

Morphology strongly influences the contact angle. Contact angle depends on the nature and surface charge of composites. Low surface charge can be attributed to composites with TiO<sub>2</sub>, in contrast to the composites with LDPE and HDPE. Sample obtained at 240 °C have the lowest water wettability.

## References

- [1] C.A., Harper, Handbook of Plastics, Elastomers, and Composites, 3rd edition, McGraw-Hill Inc., New York, 2003, p. 134.

- [2] L.A. Utracki, *Polymer Alloys and Blends. Thermodynamics and Rheology*, Hanser Publishers, Munich, 1990, p. 90.
- [3] Y. Mori, *Colloids Surf. A: Physicochem. Eng. Aspects* 311 (2007) 61–66.
- [4] A. Drechsler, C. Bellmann, A. Synytska, N. Petong, K. Grundke, M. Stamm, J. Reichelt, O. Wunnicke, *Colloids Surf. A: Physicochem. Eng. Aspects* 311 (2007) 83–92.
- [5] C. Vladuta, L. Andronic, M. Visa, A. Duta, *Surf. Coat. Technol.* 202 (2008) 2448–2452.
- [6] C. Vladuta, C. Cerbu, A. Duta, *Proceedings of the International Symposium on Shear Behavior and Mechanisms in Materials Plasticity*, Nancy, France, 2007.