

## Acid–base properties of polyethylene composites with clays

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**ABSTRACT:** We report on the surface energy characteristics of composite materials based on low-density polyethylene with addition of bentonite and organic clay. Investigated were the surface free energy, its components and parameters by wetting methods according to Berger, spatial method, and method of nonlinear systems. The determined characteristics were carried out by the selective wetting conditions for the individual constituents of the composition, including the clay powder. The thermal, mechanical, and morphological properties of obtained composites were investigated. The possibility for predicting the surface properties of composite materials based on component-wise analysis was demonstrated. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43629.

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### INTRODUCTION

The composite materials based on polymers with clay powder are widely used since the 90s in packaging, automotive and aircraft, as well as in the cable industry. As a result of a good exfoliation of layered structures in a polymer matrix the clay polymers composites are often regarding to nanocomposites.<sup>1,2</sup> Despite the fact that these materials possess a complex of useful properties, it is relatively difficult to obtain a well-exfoliated nanocomposite structure for nonpolar polymers such as polyolefins.<sup>3,4</sup>

The effectiveness of polymer composite material is largely depends on acid–base interactions between the used polymer and the additive. The importance of acid–base interactions at the polymer–polymer or metal–composite interface is proved by several studies in recent years.<sup>5–7</sup> Therefore, the first priority for creating the new polymer composite materials is the correct assessment of surface properties to predict their ability for successful interactions and for the controlled modification of these properties. Such an assessment may be carried out by conventional wetting methods using medium-geometric approach,<sup>8</sup> the concept of van Oss-Chaudhury-Good (vOCG),<sup>9</sup> Della Volpe systems of nonlinear equations,<sup>10</sup> as well as spatial method.<sup>11</sup>

Modification of polymeric materials is performed in a wide variety of purposes e.g., for imparting desired properties to the composite or to reduce the products cost.<sup>12</sup> However, such modification is often carried out excluding the consideration of acid–base properties of the joined materials and does not always

lead to positive results. Knowledge of these properties for polymers, modifiers and substrates can help choosing the components for adhesive compounds by a scientific way that can mean significant economic benefits on creating connections with the specified characteristics. However, the prediction of possible interfacial interaction with component values and parameters of the surface free energy (SFE) is of wide practical interest.

### THEORY

Diverse component values and parameters of the surface free energy (SFE) are usually calculated by wetting processes. For this purpose, various methods can be used. Proposed in the 1980s vOCG equation<sup>9,13–15</sup> describes the work of adhesion for interactions of liquid *L* to a solid *S*, is based on the Berthelot geometric mean ratio and Kollman's quantum chemical calculations<sup>16,17</sup>:

$$W_{LS} = \gamma_L(1 + \cos \theta) = \gamma_L + \gamma_S - \gamma_{LS} \\ = 2\sqrt{\gamma_L^{LW}\gamma_S^{LW}} + 2\sqrt{\gamma_L^+\gamma_S^-} + 2\sqrt{\gamma_L^-\gamma_S^+} \quad (1)$$

$\theta$  describes a wetting contact angle between solid and liquid,  $\gamma_L^{LW}$ ,  $\gamma_S^{LW}$  are the Lifshitz - van der Waals components of liquids and solids, respectively. The values  $\gamma^+$  and  $\gamma^-$  as electron-acceptor and electron-donor properties, describes according to Lewis the acid and base parameters of the SFE.

The SFE and work of adhesion satisfy the principle of additivity [eqs. (2) and (3)]:

$$\gamma = \gamma^{LW} + \gamma^{AB}, \quad (2)$$

$$W_a = W_a^{LW} + W_a^{AB}. \quad (3)$$

Hence can be written,

$$\gamma^{AB} = 2\sqrt{\gamma^+ \gamma^-}, \quad (4)$$

$$W_{12}^{AB} = 2\sqrt{\gamma_1^- \gamma_2^+} + 2\sqrt{\gamma_1^+ \gamma_2^-}. \quad (5)$$

The use of vOCG theory requires the knowledge of acid and base parameters for liquids and solids. For correct calculation of these parameters Della Volpe proposed a nonlinear modification of vOCG by solving a system of nonlinear equations<sup>18</sup>:

$$\begin{cases} \gamma_{L,i} = \gamma_{L,i}^{LW} + 2\sqrt{\gamma_{L,i}^+ \gamma_{L,i}^-}, \quad \forall i=1 \dots L \\ \gamma_{S,j} = \gamma_{S,j}^{LW} + 2\sqrt{\gamma_{S,j}^+ \gamma_{S,j}^-}, \quad \forall j=1 \dots S \\ \gamma_{L,i}(1+\cos\theta_{i,j}) = 2\left(\sqrt{\gamma_{L,i}^{LW} \gamma_{S,j}^{LW}} + \sqrt{\gamma_{L,i}^+ \gamma_{S,j}^-} + \sqrt{\gamma_{L,i}^- \gamma_{S,j}^+}\right) \end{cases} \quad (6)$$

Here is  $L$  and  $S$  a number of liquids and solids, respectively. The values for SFE  $\gamma_{L,i}$  are known from the literature and the contact wetting angle  $\theta_{ij}$  can be determined experimentally. Such systems are usually solved using the methods of multivariate optimization. But in the case of large systems of nonlinear equations such methods do not provide a sustainable and unique solution. To remedy these shortcomings, we proposed to convert vOCG eq. (1) to the plane of the equation  $z = Ax + By + C$ ,<sup>11</sup> namely:

$$\frac{\gamma_L(1+\cos\theta)}{2\sqrt{\gamma_L}} = \frac{\sqrt{\gamma_L^{LW}}}{\sqrt{\gamma_L}} \cdot \sqrt{\gamma_S^{LW}} + \frac{\sqrt{\gamma_L^+}}{\sqrt{\gamma_L}} \cdot \sqrt{\gamma_S^-} + \sqrt{\gamma_S^+} \quad (7)$$

This equation represents the equation of a plane, with  $A = \sqrt{\gamma_S^{LW}}$ ,  $B = \sqrt{\gamma_S^-}$ ,  $C = \sqrt{\gamma_S^+}$ .

By using the known values of test liquids  $\gamma_L$ ,  $\gamma_L^{LW}$ ,  $\gamma_L^+$  and  $\gamma_L^-$ , as well as the cosines of contact angles for surface wetting tested by these liquids, a plane can be plotted by multivariate approximation in coordinates:

$$\left( \frac{\sqrt{\gamma_L^{LW}}}{\sqrt{\gamma_L}}; \frac{\sqrt{\gamma_L^+}}{\sqrt{\gamma_L}}; \frac{\gamma_L(1+\cos\theta)}{2\sqrt{\gamma_L}} \right)$$

In this way the method allows the calculation of  $\gamma_S^{LW}$ ,  $\gamma_S^+$  and  $\gamma_S^-$  for investigated solids.

1991 E. Berger proposed a modification of the Owens-Wendt geometric mean approach<sup>8</sup> for the determination of the SFE components. In this method, the solid surface acidity (for metals or polymers) can be determined using seven test liquids. Two of liquids have the acid, and another two have basic character according to Lewis.<sup>19</sup> Other liquids are chosen randomly. Used test liquids pairs have very similar values  $\gamma_L^{AB}$  and  $\gamma_L^{LW}$  (phenol and aniline as Lewis acids, glycerol and formamide as Lewis bases). If there were no acid–base interaction between the substrate and the test liquid the data pair would have approximately the same contact angles and also the same calculated values  $\gamma_S^{AB}$ , defined for aniline and phenol, glycerol, and formamide. But this does not correspond to reality.

The difference in  $\gamma_S^{AB}$  for acids and bases, calculated by the formula (8) determines the surface acidity:

$$D = 2 \left[ \sqrt{\gamma_S^{AB}(\text{aniline})} + \sqrt{\gamma_S^{AB}(\text{formamide})} \right] - 2 \left[ \sqrt{\gamma_S^{AB}(\text{phenol})} + \sqrt{\gamma_S^{AB}(\text{glycerol})} \right] \quad (8)$$

The value  $D > 0$  corresponds to the acid and  $D < 0$  to the basic character of the surface.

## EXPERIMENTAL

### Materials

The low density polyethylene (PE-LD) (Kazanorgsynthesis, Kazan, Russia) was used as the polymer matrix.

As dispersed additives were used:

- The organic nanoclay Cloisite 10A, natural montmorillonite with a quaternary ammonium salt, with an average particle radius of  $5.5 \times 10^{-6}$  m, manufacturer Southern Clay Products Inc. (Gonzalez, USA).
- The Bentonite Bentokam from Berezovsky deposit (Kazan, Russia) (TU 39-0147001-105-93) with an average particle radius of  $5.5 \times 10^{-6}$  m.

Samples of unmodified polymers and composite materials were prepared by mixing on a two roll mill for 4 to 5 min. Processing temperature was 135 °C and similar for all formulations. The rotational speed of the rolls was 12.5 m/min, with friction ratio 1 : 1.2. To relieve the internal stress of prepared composites, the compound was stored for 24 h at normal conditions according to DIN EN ISO 291:2008-08 and then pressed at a temperature of 100 °C for 5 min. with afterwards cooling for 10 min.

As a composite material, samples of PE-LD with 4, 5, 10, and 20 wt % organoclay and 4, 10, and 20% wt. bentonite were prepared. All formulations were prepared without the addition of a compatibilizer.

### Methods

**Wetting.** The contact angle was determined according to DIN 55660-2 by sessile drops with the drop shape analyzer EasyDrop (Kruss GmbH, Hamburg, Germany). The value  $\theta$  was calculated as the average of at least five measurements. In this way the error in determining of  $\cos\theta$  was amounted to at least 5%. Surface free energy and its components, as well as acid and base parameters are determined using the theory of nonlinear systems by vOCG, Della Volpe, the spatial method, and the Berger method based of on the theory of Owens-Wendt.<sup>8,9,11,18</sup>

**Test Liquids.** For the experiments the following liquids were used: aniline (Merck KgaA, Darmstadt, Germany); a-bromonaphthalene (Panreac 1, Barcelona, Spain); formamide (Panreac 1, Barcelona, Spain); diiodomethane (Acros Organics, Geel, Belgium); glycerol (Ecos, St. Petersburg, Russia); dimethylsulphoxide (DMSO) (Ecos, St. Petersburg, Russia); distilled water; saturated water solution of  $K_2CO_3$ ; ethyleneglycol (Ecos, St. Petersburg, Russia); phenol (liquified with 12% water) (Kazanorgsynthesis, Kazan, Russia); and dimethylformamide (DMFA) (Ecos, St. Petersburg, Russia). The purity was for all liquids of p.a.

**Atomic Force Microscope.** To determine the roughness of the samples and the content of clay particles on the surface as well

**Table I.** Features and Options SFE Clay Powder

Surface	$\gamma_s^{LW}$	$\gamma_s^+$	$\gamma_s^-$	$\gamma_s^{AB}$	$\gamma_s$
Organoclay	146.7	1.1	0.0	0.0	146.7
Bentonite	14.5	23.1	16.4	38.9	53.4

as the suitability of the samples for using the wetting methods, the atomic force microscope MultiModeV, (Veeco Instruments Inc., San Jose, USA) was used.

**Thermal Analysis.** The TGA and DSC studies were carried out with thermal analyzer SDT Q600 at a temperature range from 20 to 750 °C at a heating rate of 10 °C/min in air as process gas.

**Scanning Electron Microscope (SEM).** Surfaces of polymer composites, were investigated in scanning electron microscope Merlin (Carl Zeiss, Oberkochen, Germany) in transmission using STEM-detector and setting the accelerating voltage on 25 keV. Sample preparation was carried out by cutting microtome Leica UC7. The slice thickness was amounted to 100 nm. The sections were mounted on 400 mesh 3 mm copper grid.

## RESULTS AND DISCUSSION

Creation of an “ideal” composite material, such meets all the specific requirements, remains an unsolved problem. Obviously a scientific approach to solve such problems must be applied for a projected component selection of the polymeric material.

Polymer composite materials contain often many ingredients in their formulation. Based on this, diverse various interactions between the polymeric matrix and ingredients occur. These interactions take place at different energies, extending from chemical to physical nature. Each individual component contributes changes in thermal and mechanical properties as well as in surface free energy and acid–base properties of the composite.

### Characteristics of the Dispersed Additives

The identified parameters of SFE the Lifshitz - van der Waals  $\gamma_s^{LW}$  and acid–base  $\gamma_s^{AB}$  components, as well as the acid  $\gamma_s^+$  and base  $\gamma_s^-$  parameters of bentonite and organoclay are summarized in Table I. Measurements were carried out with a selective wetting method in a neutral hydrocarbon with test liquids.<sup>20</sup>

According to achieved results the bentonite has hydrophilic, and organoclay hydrophobic properties. Due to the fact that the exchange of montmorillonite complex component represented mainly by alkaline cations, the acidic properties with parameter  $\gamma_s^+ = 23.1$  mJ/m<sup>2</sup> predominate (vs. basic parameter  $\gamma_s^- = 16.4$  mJ/m<sup>2</sup>).<sup>1,21</sup> Evaluation of the surface free energy and the acid-

base properties for organoclay is also in a good agreement with literature published data. The modified bentonite as a result of saturation of the activated raw clay with the quaternary ammonium salt, change hydrophilic properties to hydrophobic, as in the modification in montmorillonite layers the interlayer gap hydrate-ionic water displaced with organic cations.<sup>21</sup>

Analyzing the data in Table I is to notice the extremely low value of Lifshitz - van der Waals component for bentonite. The explanation of this fact is the reduction of SFE for hydrophilic solid by adsorption the moisture from the atmosphere, which is not displaced by a neutral hydrocarbon.

### Characteristics of the Modified Polyethylene

Thermodynamic characteristics of unmodified PE-LD were assessed with three methods mentioned above: Berger method, the Della Volpe method of nonlinear systems and spatial method. This was done due to remove the disadvantages of the different method for evaluating characteristic. By analyzing the summation of results obtained by diverse methods, it is possible to evaluate the nature of the surface materials more reliably. The obtain results are shown in Table II.

As a result of the thermal oxidation during the formation, the surface of PE-LD becomes a slightly acidic nature. This is confirmed by all three methods. According to the Berger method  $D$  is greater than zero ( $D = 1,4$ ). The acid parameter in the calculation with method of nonlinear systems and spatial methods is higher as basic with  $\gamma^+ = 4,2$  (with the method of non-linear systems) and  $\gamma^+ = 1.8$  (with spatial method).

### Surface Characteristics of Polyolefin Composites

To analyze the topography of the surface (roughness, heterogeneity) the composite material samples made of PE-LD with clay powder were investigated by means of semi-contact atomic force microscopy. The obtained data are presented in Figures 1 and 2.

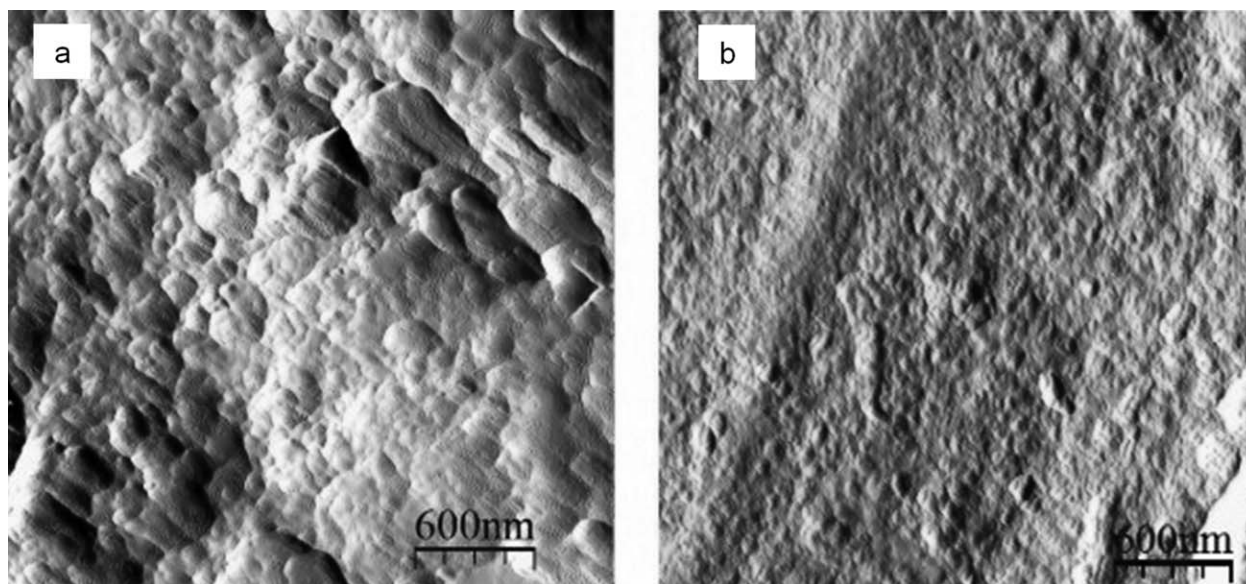
According to the distribution of height obtained for  $2 \times 2 \mu\text{m}$  on composite surface (Figure 2), the dimensions of the sample roughness with bentonite does not exceed 400 nm, while for the sample with organoclay the surface roughness does not exceed 50 nm. According to the Summ and de Jen approach<sup>22,23</sup> the investigated surface can be considered as sufficiently smooth. This allows the application of wetting methods for measurement of the surface energy characteristics.

Table III shows the obtained values of the thermodynamic surface characteristics defined by Berger method, the method of non-linear systems Della Volpe and spatial method for the modified PE-LD.

The presence of both bentonite and organoclay in composites does not greatly affect the composite surface properties. As can

**Table II.** Surface Energy Characteristics of PE-LD

Method	$\gamma_s^{LW}$	$\gamma_s^+$	$\gamma_s^-$	$\gamma_s^{AB}$	$\gamma_s$	$D$
Berger method	34,4	-	-	4,2	38,6	1,4
Systems of nonlinear equations (Della Volpe)	35,2	4,2	0,9	3,9	39,1	-
Spatial method	35,4	1,8	1,1	2,9	38,3	-



**Figure 1.** Surface images: (a) PE-LD modified with 20% bentonite, (b) PE-LD modified with 20% organoclay.

be seen in Table III the acidic nature of the polyethylene surface slightly increases with the addition of bentonite, which has predominantly acid properties. In contrast the adding of organoclay reduces the surface acidity to nearly zero (by Berger method). Similar results provide a method of nonlinear systems. In this calculation method the acidity is more pronounced by a pure polyethylene sample ( $\gamma^+ = 4.2$ ), as well as composites with bentonite (4.3 and 5.5 for 10 and 20 wt % additive concentration, respectively).

As follows from the results, the acid and base parameters of organoclay composite are similar in all cases, generating as a result the nonpolar surface. But it contains both acid and base centers (e.g., a sample with 5% organoclay with  $\gamma^+ = 2.9$ , and  $\gamma^- = 2.7$ ). These values can be reduced by increasing content of organoclay.

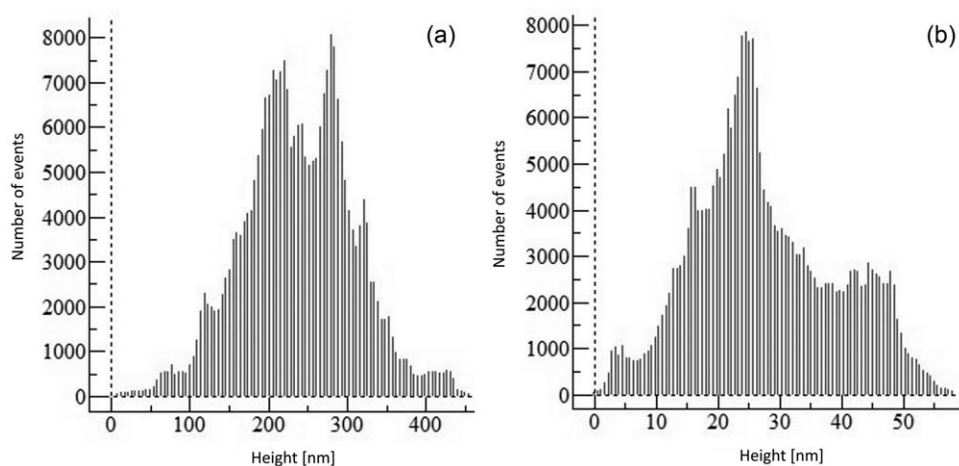
The results of the spatial method, are slightly differing in numerical terms, but remain the same pattern. The surface of

the unmodified PE-LD has predominantly acid parameter, and this acidic property becomes more significant with the addition of bentonite. In composites with organoclay acid and base parameters fluctuate within the unit, which leads to integral neutral surface.

Thus, all methods provide consistent results, from which it can be concluded:

- Surface PE-LD and bentonite has acidic properties;
- The surface of PE-LD and organoclay is neutral, its acid and base parameters are close to each other;
- The presence of clay powder in the composite material affects only slightly on the surface properties.

On the basis of obtained the results for each of the materials individually: bentonite, organoclay and PE-LD, we calculated the work of adhesion ( $W_a$ ) and SFE of composites PE-LD-bentonite and PE-LD-organoclay. Since in this case the



**Figure 2.** Histograms of surface with region  $2 \times 2$  mm: (a) PE-LD modified with 20% bentonite, (b) PE-LD modified with 20% organoclay.

**Table III.** Components and Parameters of SFE for Investigated Composites

Composites	Parameters acc. to Berger method			Components and parameters obtained with a method of non-linear systems			Components and parameters obtained with spatial method		
	$\gamma^{LW}$	$\gamma^{AB}$	$D$	$\gamma^{LW}$	$\gamma^+$	$\gamma^-$	$\gamma^{LW}$	$\gamma^+$	$\gamma^-$
PE-LD/bentonite 10%	32.6	4.5	1.6	33.6	4.3	0.3	30.7	4.3	0.6
PE-LD/bentonite 20%	32.2	7.0	1.8	34.2	5.5	1.4	34.8	4.7	1.3
PE-LD/organoclay 5%	31.6	5.1	0.3	32.3	2.9	2.7	36.9	1.3	0.5
PE-LD/organoclay 10%	34.5	4.5	0.2	33.6	2.0	2.0	34.4	0.8	1.2
PE-LD/organoclay 20%	32.5	4.2	0.0	32.6	1.9	1.9	36.9	0.3	0.9

contribution to the interaction of the adhesive will generally be dictated by specific interactions (due to a range of molecular dispersion forces), the main informative value here is  $W_a$ . For bentonite:

$$W^{AB} = 2 \left( \sqrt{\gamma_1^+ \gamma_2^-} + \sqrt{\gamma_1^- \gamma_2^+} \right) = 21.1 \text{ mJ/m}^2$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - W_a = 25.2 \text{ mJ/m}^2$$

For organoclay:

$$W^{AB} = 2 \left( \sqrt{\gamma_1^+ \gamma_2^-} + \sqrt{\gamma_1^- \gamma_2^+} \right) = 2.3 \text{ mJ/m}^2$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - W_a = 38.5 \text{ mJ/m}^2$$

As follows from the obtained data,  $W^{AB} = 21.07 \text{ mJ/m}^2$  for bentonite composite is almost an order of magnitude higher than for PE-LD with organoclay ( $W^{AB} = 2.27$ ). But the interfacial energy of the latter composite is higher than the first. These data suggest that apart from the processes intercalation and exfoliation of clay and to consider the surfaces as hard and smooth, the wetting of bentonite particles with the polymer melt should be better ( $\gamma_{12} \text{ bentonite} < \gamma_{12} \text{ organoclay}$ ) and acid–base interaction of bentonite with the PE-LD is higher than with organoclay. This verify also the cohesive strength of the composites. The average tensile strength of the bentonite was with

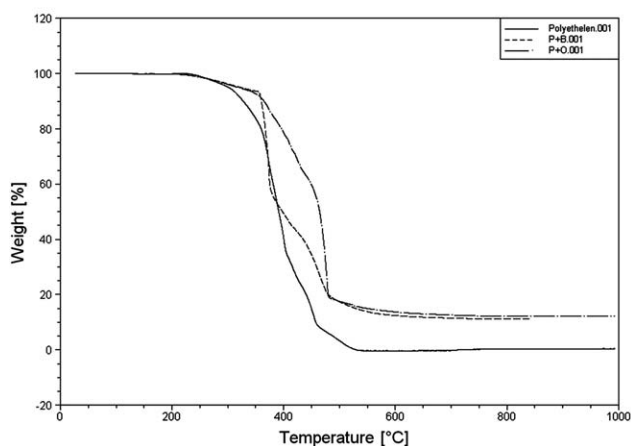
$9.91 \pm 0.15 \text{ MPa}$  was slightly higher than with organoclay ( $\sigma = 9.37 \pm 0.13 \text{ MPa}$ ).

The results show, that the surface of the organoclay composite is smoother than bentonite composite. This may be due to the different distribution of the powder within the matrix, and their various thermal properties. To clarify the issue, the studied composites were subjected to DSC and TGA analysis.

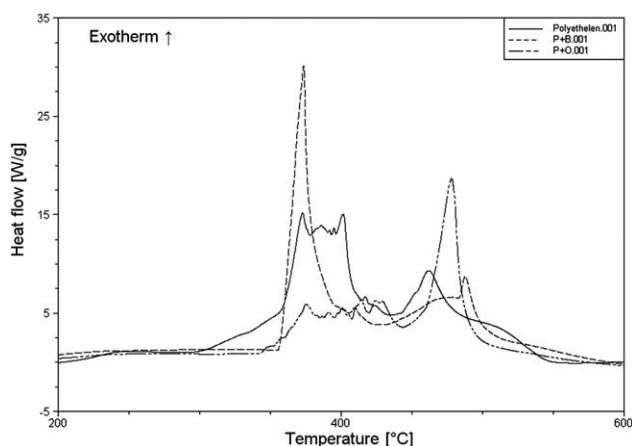
#### Thermal Analysis of Composites

The addition of the organoclay in the polymer matrix, can improve the thermal stability of the polymer.<sup>3,24,25</sup> This fact indicates the interfacial interaction between the polymer and the dispersed additive. To clarify this issue we studied samples of PE-LD with 20% bentonite and 20% organoclay by DSC and TGA.

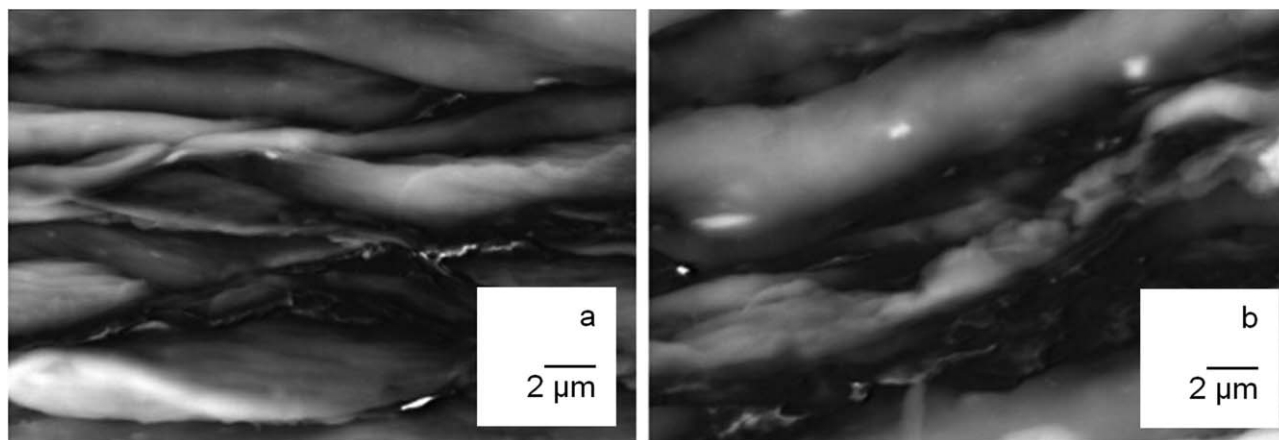
First of all, we note that conventional thermal effects are expected on origin modifiers by investigation with DSC and TGA,<sup>21</sup> because of minimal amount of adsorbed water in the clay powder. The degradation of unmodified PE-LD begins after 300 °C and occurs in two stages. Nearly the half of the mass loss occurs at 390 C (Figure 3, solid line). According to Dolegel,<sup>26</sup> the polyethylene degrades first to low molecular weight polyethylene, and at higher temperature the liquid degradation products arise with significant amounts of gases. For investigated composites we could see two related processes described above,



**Figure 3.** TGA curves. PE-LD (solid line), PE-LD with 20% bentonite (dotted line), and PE-LD with 20% organoclay (large dotted line).



**Figure 4.** DSC curves. PE-LD (solid line), PE-LD with 20% bentonite (dotted line), and PE-LD with 20% organoclay (large dotted line).



**Figure 5.** Images of the PE-LD with 4% bentonite (a) and PE-LD with 4% organoclay (b).

the DSC curves main peaks at 372 °C and 462 °C, respectively (Figure 3 solid line).

Presented results indicate that in the presence of bentonite the destruction begins later and faster. This indicates a sharp decline in the TGA curve, which become more apparent in the above two stage temperature ranges about 340–380 °C and 450–500 °C with weight loss 42 and 43%, respectively (Figure 3, dotted line). Maximum exothermal effect in the final stage of degradation is shifted from 462.2 °C to 487.8 °C (Figure 4, dotted line), that may be indicative for increasing the thermal stability of certain polyethylene structures.

In the presence of organoclay the intensities of two previously described exothermal peaks are redistributed (Figure 4). The determined spent heat quantity for organoclay composite, for first stage of degradation was 1321 J/g, and for the second 1990 J/g. For the composite with bentonite lay the heat quantities at 3014 and 1088 J/g, respectively. For the unmodified PE-LD polymer, these values are 3508 and 1563 J/g, i.e., closer to composition containing bentonite. The first phase of destruction of pure polyethylene covers the temperature range from about 348 to 434 °C (about 86 °C). For the bentonite composite this stage lasts from 355 to 420 °C, i.e., is reduced by 20 °C.

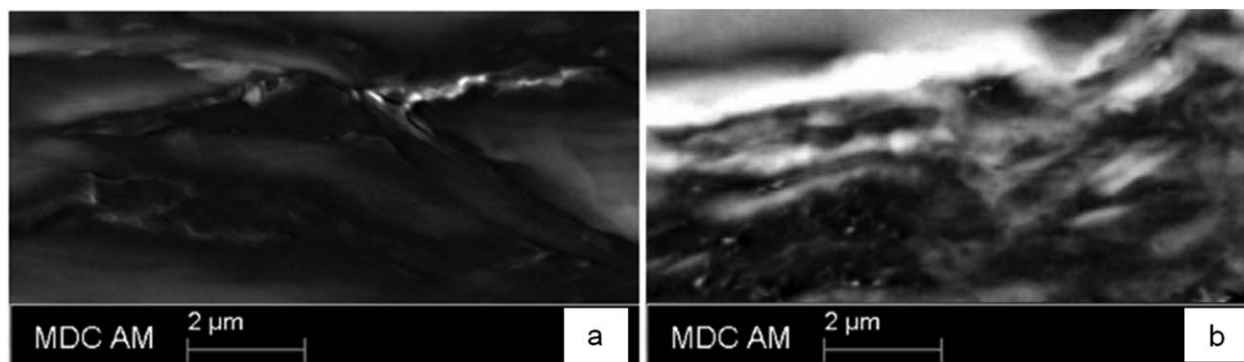
For the composite PE-LD with organoclay this stage is expanding from 355 to 450 °C. For such composites this can be facilitated as described in the literature by Hofmann's elimination reaction. The result of a alkylammonium cation destruction (which begins

shortly after the 200 °C and finishes to 350 °C) further provoke the destruction of the polymer matrix.<sup>27,28</sup> In this case a sample with organobentonite the main weight loss occurs at about 80 °C later than that of the unmodified PE-LD (Figure 3, large dashed line), while the sample with bentonite similar process occurs substantially simultaneously with the pure PE-LD. It turns out that the degradation on the polymer backbone in the presence of an organoclay begins later occurs to a lesser extent. An important role plays here also the well-known effect of polymer intercalation in the interlayer space of montmorillonite. The composite with organoclay is more thermally stable than pure polyethylene.

The influence of clay (especially organoclay) on thermo-oxidation and thermo-destructive behavior of composite is certainly available. This is not only a consequence of the barrier layers effects of clay for the diffusion of oxygen into the polymer matrix,<sup>3</sup> but also the result of good thermodynamic compatibility for hydrocarbon chain of polyethylene and clay modifier. It is also possible that thermal oxidation of the polymer occurs during formation of the sample causes the polar oxygen-containing groups that can form hydrogen bonds with the functional groups of active clay.

#### Analysis of Composite Materials by Transmission Electron Microscopy

The morphology of the composites, analyzed by transmission electron microscopy show Figures 5 and 6. The introduced



**Figure 6.** Enhanced image structure of the samples PE-LD with bentonite (a) and PE-LD with organoclay (b).

images of the surface are cross sections of 80–100 nm thick films. According to the submitted images tactoids with size from 1.0 to about 16.0  $\mu\text{m}$  for bentonite and not more than 5.0  $\mu\text{m}$  for the organoclay in polymer composites are present. Because the original size of the bentonite particles are in the range of 1.4–28.0  $\mu\text{m}$  with an average particle radius of 5.5  $\mu\text{m}$  and an organoclay for the same size is 1.0–13.0  $\mu\text{m}$  and 5.5  $\mu\text{m}$ , it can be concluded that the dispersion of the organoclay in the polymer is better. Its particles are noticeably smaller; therefore, there is a partial exfoliation of clay.

On the photographs are visualized the signs of polymer intercalation in the interlayer space of montmorillonite (Figure 6). The observed pattern resembles periodic bicontinuous dispersed structure<sup>29</sup> in which the clay platelets and the polymer layers have a thickness of the order of hundreds of nanometers. Moreover, for the sample with organoclay such structures can more be considered than in the presence of bentonite. The layer thickness is usually in the range of 170–300 nm, but the organoclay composite has a striped structure finer to 100 nm in a cross section [in Figure 6(b)].

With the used method of preparing composites without using the compatibilizer it is difficult to achieve a high degree of clay dispersion and peeled structure, i.e. complete exfoliation in the polymer.

Based on SEM analyzing, we can conclude that:

- The degree of the organoclay dispersion in polyethylene is rather than bentonite. Organoclay tactoids are smaller than the particles in original size. The particles of organoclay are increasingly exfoliated.
- Alternating layered structures in the composite polymer—clay are observed more frequently to polymer—organoclay composite. Organoclay composites have more thin layers.
- The additive particles are completely surrounded by polymer. In its original form, there is no presence of clay on the surface of the composite.

## CONCLUSIONS

Analyzing the influence question of the observed morphology for the both composites on its surface properties, we can see that tactoids, intercalated structures and organoclay plates arranged substantially parallel to the film surface and through the interfacial interactions each particle is surrounded by the polymer. This leads to surface effect that, there is no clay in a native form on the surface of the composite. Therefore, a strong thermodynamics effect cannot be observed on the composite surface with a small amount of an additive (4%). This effect becomes noticeable when by adding a bigger amounts of clay (for example, in the case of adding 20% bentonite).

Organoclay is better react with PE-LD and its dispersion in the polymer is more complete. As organoclay is also a thermal stabilizer of polyethylene, in the presence of this additive less oxidation processes are expressed on the surface and the surface become the neutral properties.

In this study, we have used both inductive (from individual to general) and deductive (from general to specific) methods. In the first phase of the study, we determined the surface energy properties of the individual components of the composite - polymer and dispersed additives. In the second stage the same properties of the composite materials were evaluated. Further, based on the information of the individual components, we explain the meaning of SFE, its components and parameters for the surface of the composite material.

According to our calculations, the acid–base interaction of bentonite with polyethylene is more noticeable than with the organoclay, but the experiment shows the opposite. Obviously, this reaction is suppressed by other stronger effects (such as polymer intercalation and exfoliation of clay) for the modified clay.

Scientific prediction of SFE properties for composite materials involves inductive method of analysis. The knowledge of these properties for individual components makes it possible to predict the properties of the final product. Furthermore, the selection of the components for compounds can be produced in a scientifically manner.

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