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Low density polyethylene–montmorillonite nanocomposites for film blowing

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Abstract

Low density polyethylene nanocomposites were prepared using differently modified montmorillonite (MMT) and different compatibilizers. The best results were obtained for MMT with largest gallery distance. The most exfoliated system was further optimized for superior mechanical properties by varying the compounding condition. The criteria were mechanical properties of nanocomposites and X-ray proofs of exfoliation. The optimized nanocomposites were used for film blowing. The effect of blow ratio on mechanical properties and oxygen permeation of films was evaluated for two best nanocomposites and two films blown from pristine polyethylene. The texture of crystalline phase of blown films was analyzed by X-ray pole figure technique, SAXS and AFM. Two components of texture were detected, the first component related to the molecular orientation of polyethylene by film blowing and take-up and the second connected with the formation of free surfaces of the film. The crystallinity degree from DSC and long period determined from SAXS of polyethylene component were nearly independent of the additives. It indicated that the compatibilizer was preferentially located around clay platelets and did not enter the amorphous layers of polyethylene. Also the orientation of clay platelets was determined by FTIR using 1080 cm⁻¹ band characteristic for Si–O bonds. A clear correlation of oxygen permeativity of blown films with clay platelets orientation and degree of exfoliation was evidenced.

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1. Introduction

The market for polymer nanocomposites is estimated now for more than 200 million USD with 18% annual growth. It is expected that it will reach 55 × 10⁴ Mg by 2009 [1]. The main application fields are automotive industry, aero-spatial applications, packaging, household goods, building industry and sporting. Barriers in a broader application are the technological difficulties that arise when a desired level of improvement is expected at a low costs. Many experimental studies are undertaken in order to elucidate best ways of nanocomposite preparation and determine their application. Most
of explored nanocomposites are based on platelet nanoclays and thermoplastics, prepared by melt blending using extruders [2–7]. Montmorillonite (MMT) is most often applied because of its high specific surface and large ion exchange capacity [8,9]. However, a barrier for easy dispersion of clay platelets in most of thermoplastics is hydrophilic character of MMT. Modification of MMT is necessary in order to decrease the surface tension, decrease the wettability and making MMT organophilic [10]. Quaternary ammonium salts of fatty acids are most often used to replace the cations in the galleries [11,12]. The main weakness of those modifiers is their low thermal resistance, usually not exceeding 200–220 °C. At higher temperature a thermal decomposition of ammonium salts results in a decrease of interlayer distance and a loss of exfoliation possibility [9]. Intercalation or exfoliation occur under condition of negative change of free energy, \( \Delta F \), of the intercalation process, i.e. the penetration of polymer macromolecules into galleries and expanding the interlayer distance from \( h_0 \) to \( h \). Energy difference \( \Delta F \) can be written as

\[
\Delta F = F(h) - F(h_0) = \Delta E - T\Delta S < 0
\]

where \( \Delta E \) is the intrinsic energy change resulting from intermolecular interactions of all components of the system, \( \Delta S \) is the entropy change connected with changes in configuration of polymer macromolecules, particles of a modifier and MMT platelets while \( T \) is the temperature. The entropy change due to translation of MMT platelets is negligibly small because of their volume stability. Confinement of polymer chains in a space between MMT platelets which is less than the diameter of macromolecule gyration limits the freedom of conformational changes and possibility of relaxation, hence, the polymer intrinsic energy is changed. The entropy change is then negative and decreases further when the value of \( h \) increases. The entropy change of molecules of a modifier is positive for the range of \( h \) comparable with double distance of extended modifier chain length. It appears that for \( \Delta h = h - h_0 > 0.8 \text{ nm} \) total entropy change is negative and intrinsic energy change decides about the intercalation/exfoliation success [9,13,14]. The energy changes can be expressed in the following way [9]

\[
\Delta E = S_{m-p}^k \cdot k_{m-p} + S_{m-md}^p \cdot k_{m-md} + (S_{m-md}^k - S_{m-md}^p) \cdot k_{m-md}
\]

where \( S_{m-p}^k \) is the surface area of polymer-clay interaction after intercalation, \( k_{m-p} \) is a change in energy connected with the replacement of MMT–MMT platelets interaction for MMT-polymer interaction, \( S_{m-md}^p \) is the surface area of interaction between modifier molecules and polymer after intercalation, \( k_{m-md} \) is the energy change resulting from replacement of interaction modifier–modifier and polymer–polymer for interactions between modifier and polymer, \( S_{m-md}^k \), \( S_{m-md}^p \) are the surface area of interaction between MMT and a modifier before and after intercalation, respectively, \( k_{m-md} \) is the change in energy resulting from a replacement of interactions of MMT–MMT and modifier–modifier for interaction MMT-modifier.

The condition of \( \Delta E < 0 \) requires an increase of polar interactions, mainly base-acid on the account of non-polar. For that purpose modifiers containing such polar groups and non-polar tail are applied. In addition a dopant may be required, which should be compatible with a polymer and modifier [15,16]. A compatibilizer may have a detrimental effect on the stability of a nanocomposite as it usually decreases the thermooxidative resistance of a polymer (case of polypropylene, see [17]). For the purpose of increasing the surface area of interaction an intensive shear mixing is usually applied. Screw extruders and twin screw corrotating extruders are preferably used [7,10,18]. Longer residence time is advantageous for more efficient intercalation and/or exfoliation. The importance of shearing in intercalation and exfoliation of MMT was confirmed by several research groups and also the dependence of exfoliation efficiency on screw configuration [7].

Polymer nanocomposites with MMT have usually superior mechanical, thermal and barrier properties over pristine polymers. Improved barrier properties especially are important for packaging materials. Reduction of gas permeativity in platelet nanocomposites is usually explained as the result of a significant increase in a diffusion path because gas molecules cannot permeate through MMT platelets [9,19,20]. According to the above statement the barrier properties of a nanocomposite is influenced by: permeativity of a polymer matrix (\( P_0 \)), volume concentration of MMT in nanocomposite, \( c \), aspect ratio of MMT platelets, \( p \), orientation of MMT platelets with respect to gas diffusion direction described as an angle \( \Theta \) between diffusion direction and platelets plane. Permeativity \( P_{NC} \) of a nanocomposite is then described by the formula [9,20]:

\[
P_{NC} = P_0 \cdot f(\Theta)
\]
\[ P_{NC} = P_0 \cdot \frac{1 - c}{1 + c \cdot p \cdot (S + 1/2)/3} \]  

(3)

where

\[ S = \frac{3(\sin^2 \Theta) - 1}{2} \]  

(4)

When MMT platelets are perpendicular to the diffusion direction then \( \Theta = \pi/2 \) and \( S = 1 \) and the Eq. (3) reduces to

\[ P_{NC} = P_0 \cdot \frac{1 - c}{1 + c \cdot p/2} \]  

(5)

For a typical aspect ratio of MMT platelets of 500 and concentration of 3 vol.% an expected permeability is eight time lower than the value for a polymer alone. For the parallel orientation, i.e. for \( \Theta = 0 \), \( S = -1/2 \), we have a decrease in permeability at the level of concentration of MMT only, described by the following form:

\[ P_{NC} = P_0 (1 - c) \]  

(6)

If the exfoliation of MMT is not full the aspect ratio should be adjusted, respectively. The Eqs. (3), (5) and (6) are for flawless systems, however, usually the orientation is not perfect, there are defects like bubbles, holes and quartz impurities in MMT. Such imperfections are dramatically influencing the barrier properties, especially for films having the thickness comparable with sizes of defects. Also the solubility of gas was not taken into account in the above equations [21]. Nevertheless, from the presented consideration it follows that concentration of MMT, degree of dispersion and orientation have significant influence on barrier properties for gases of a nanocomposite. The presence of clay platelets and their orientation modify also the supermolecular structure of a polymer. Since crystalline polymer lamellae are impermeable for gases their orientation is also very important.

The aim of the study was to investigate the effect of clay platelet orientation and resulting supermolecular structure of low density polyethylene (LDPE) on oxygen permeativity. The preferred means of orientation was film blowing. The brands of MMT, type of a compatibilizer and blending conditions were varied in order to optimise the composition for film blowing. Also the parameters of film blowing were varied in order to establish their influence on supermolecular structure of polyethylene, MMT platelets orientation and selected properties of nanocomposite films.

2. Experimental

2.1. Materials and sample preparation

Low density polyethylene (LDPE) MALEN E GGNX 23D022, MFR = 1.6–2.5 g/10 min (190 °C, 2.16 kg), stress at fracture 14 MPa (by BASELL-Orlen Polyolefins Plock, Poland) was used throughout the study. Several organomodified MMT including:

(a) Cloisite 15A: \( d_{001} = 3.15 \text{ nm}, \text{ CEC} = 125 \text{ meq}/100 \text{ g}, \text{ density} = 1.66 \text{ Mg/m}^3 \), modified by quaternary ammonium salt of fatty acids by Southern Clay Products, Gonzales, TX, USA,

(b) Nanocor I30P: \( d_{001} = 2.2 \text{ nm}, \text{ CEC} = 95 \text{ meq}/100 \text{ g}, \text{ density} = 1.9 \text{ Mg/m}^3 \), modified by quaternary ammonium salt of fatty acids, by Nanocor Inc., USA,

(c) Bentonite special: \( d_{001} = 2.1 \text{ nm}, \text{ modified by didecyl-dimethylammonium chloride, by ZGH Zebiec, Poland} \),

were used.

The following compatibilizers were applied:

(a) Orevac CA18365; MFR = 2.5 g/10 min (190 °C, 2.16 kg), by Arkema Inc.

(b) Fusabond EMB 226D; MFR = 1.5 g/10 min (190 °C, 2.16 kg), by DuPont.

(c) Elvaloy AC 1820; MFR = 8.0 (190 °C, 2.16 kg), by DuPont.

A series of samples of nanocomposites and samples for comparison were prepared by melt blending. The amount of compatibilizer was set at 15 wt.% while the amount of MMT was maintained at 5 wt.% The list of samples is presented in Table 1.

Nanocomposites were compounded using a double screw corotating extruder \((D = 20 \text{ mm and } L/D = 40)\) type BTSK 20/4 OD by Bühler Co. The temperature profile 150, 160, 170, 170, 170 °C, screw rotation speed of 250 min\(^{-1}\) and screw configuration as in Fig. 1 are applied as in a previous study [22]. For further optimization the temperature profile, screw configuration and screw speed were varied as described in Section 3. Montmorillonite was dried for 3 h at 60 °C, then premixed with pellets of polymer and compatibilizer and fed to the extruder. Extrudate was cooled down in air at 23 ± 3 °C and at relative humidity 48 ± 3% and pelletized.
Samples for mechanical tests according to EN ISO 294-1 were injection moulded using Battenfeld type PLUS 35/75, UNILOG B2 injection moulding machine.

The study of film extrusion and blowing was performed on a single screw extruder. The equipment used was PlastiCorder PLV 151 by Brabender consisting of a single screw extruder with screw diameter of 19 mm, \( L/D = 25 \) and compression ratio of 3:1. The extruder was equipped with a blowing head having an orifice of 14 mm in diameter. The other parameters of the process were: the temperature profile of the extruder: 150, 160, 175 °C, the temperature of blowing head 165 and 175 °C, the temperature of cooling air: 22±2 °C, its relative humidity: 48 ± 3%. The extruder screw rotation speed was varied: 30 or 45 min\(^{-1}\), the take-up velocity was set to such a rate to maintain the longitudinal draw ratio of 8:1 in either case and similar film thickness. The blowing ratio was set to 3:1 or 6:1, respectively.

2.2. Sample properties and structure

Mechanical properties were determined according to EN ISO 527 including tensile modulus, tensile strength, stress and strain at fracture. The gauge length of the samples was 50 ± 0.5 mm type 2. TIRATEST 27025 tensile testing machine was used.

Melt flow ratio (MFR) according to EN ISO 1133 was determined using capillary plastometer Dynisco, LMI 4003 at 190 °C, under load of 2.16 kg.

2.2.1. WAXS

Computer controlled X-ray diffractometer equipped with a pole figure attachment, coupled to a sealed-tube source of filtered Cu K\(\alpha\) radiation \( \lambda = 0.1541 \) nm, operating at 50 kV and 30 mA (Philips), filtered by Ni filter and electronically, was used for X-ray measurements. Dispersion of MMT platelets in LDPE matrix was determined by diffraction in transmission mode within 2\(\Theta\) angles from 1 to 9°. The divergence slit opening was 0.05°. Samples of nanocomposites for dispersion determination were grinded to a powder form in order to prepare X-ray powder sample between two Capton thin films. The details of the procedure are described elsewhere [23].

The texture of blown films was studied using the X-ray pole figure technique (for overview of this technique see e.g. Ref. [24]). The specimens were prepared by stacking of several 20 × 20 mm pieces of a film to form a 0.5 mm thick sandwich. Each film piece was aligned in plane to match exactly the blowing and elongation directions. The (110), (200) and (020) crystal planes of orthorhombic form of PE were analyzed (diffraction maxima centered around 2\(\Theta\) = 14.2°, 16.1° and 21.1°, respectively) and the respective pole figures were constructed. Experimental diffraction data were corrected for background scattering, sample absorption and defocusing of the beam. All pole figures were plotted with the POD program (Los Alamos National Lab, NM). Other details of the experimental procedure were described elsewhere [23].

2.2.2. SAXS

Lamellar structure of raw and blown films was probed by two-dimensional small angle X-ray scattering (2D SAXS). The 1.1 m long Kiessig-type camera was equipped with a tapered capillary collimator (X-ray optical systems) combined with additional pinholes (300 µm in diameter) forming the beam, and an imaging plate as a detector (Fuji). The camera was coupled to a X-ray source (sealed-tube, fine point Cu K\(\alpha\), Ni-filtered radiation, operating at 50 kV and 40 mA; Philips). Exposed imaging plates (usually 3 h) were read with Phosphor.
Imager SI scanner and ImageQuant software (molecular dynamics). Long periods (LP) in the direction of interest were determined from appropriate one-dimensional sections of 2D patterns. LP was calculated using the Bragg’s law from the position of the maximum of the curve adjusted for background and Lorentz correction.

Thermal properties were studied using thermogravimeter STA 625 by Polymer Labs. Ten milligram samples were heated from 20 to 600 °C with the rate of 20 °C/min in air and in nitrogen. A differential scanning calorimeter DSC model TA 2920 by TA Instr. was used for determination of melting temperature and melting enthalpy. The measurements were performed according to EN ISO 11357-1 and 11357-3 within the temperature range from 10 to 180 °C in nitrogen atmosphere with the heating rate of 10 °C/min.

2.3. Atomic force microscopy

The inner surface of blown films was investigated using a Nanoscope IIIa atomic force microscope (Digital Instruments/Veeco) operated in a tapping mode. Rectangular silicon cantilevers model RTESP7 (Nanosensors, Wetzlar-Blankenfeld, Germany) were used throughout the study. The AFM was calibrated laterally using the standard calibration grid purchased from Veeco. Height calibration was performed using freshly cleaved highly oriented pyrolytic graphite (HOPG, SPI Supplies) surface with thermally etched monolayer pits (step height 0.335 nm).

2.4. Fourier transform infrared spectroscopy

For the determination of orientation of nanoclay platelets the infrared absorption spectra were obtained with an ATI Mattson Infinity FT spectrometer system with a resolution of 2 cm⁻¹. A sample of blown film was placed on a tilted stage and an IR polarizer (KRS-5 wire grid polarizer by Graseby Specac) was used to record the tri-chroic spectra. The final spectra were averaged over 32 scans.

2.5. Blown films properties

Blown films were subjected to exhausting investigations typical for packaging films including:

1. Tensile properties – samples prepared according to EN ISO 527-3 oar-shaped type 5, gauge length 25 mm, total length 70 mm, experiments according to EN ISO 527-1, tensile testing machine TIRA-TEST 27025, the elongation rate 100 mm/min.
2. Tearing resistance – samples prepared according to EN ISO 527-3, measurements according to EN ISO 6383-2, tensile testing machine TIRA-TEST 27025, the elongation rate 100 mm/min.
3. Oxygen permeativity – according to ASTM D 1434-1988 method V (volumetric), capillary 0.5 mm, temperature 20 ± 0.5 °C, pressure difference 100 – 95 psi, the results were rescaled to normal conditions, i.e. 0 °C and atmospheric pressure 1 atm, the equipment CS 135C by Custom Scientific Instruments.
4. Free surface energy – by direct determination of the wetting angle, the following liquids were used: double-distilled water, glycerol and methylene diiodide, the goniometer used was type G10 by Krüss GmbH, volume of the droplet was each time 3 mm³, the free surface energy was calculated from wetting angle applying van Oss-Gooda (see for example Ref. [25]) method.
5. Degree of crystallinity was determined by DSC by heating with the rate of 10 °C/min.

3. Results

3.1. Selection of nanoclay and compatibilizers

The results of determination of mechanical properties of the set of samples from Table 1 are collected in Table 2. The analysis of the data from Table 2 leads to the following statements:

- Most of nanocomposites samples exhibit lower melt flow index than pristine LDPE subjected to the same rheological treatment. The smallest change is for composites with Elvaloy AC 1820 compatibilizer which results probably from its high melt flow index (8 g/10 min).
- Differences in tensile properties are not large for all nanocomposites, except for PE7 for which the tensile strength and the tensile modulus are 20% and 40% larger than for the reference sample PE1, respectively. Together with low value of melt flow index and high strain at fracture it is suggestive that the dispersion of MMT platelets is most effective in that nanocomposite (PE7).
- All samples containing MMT Cloisite 15A show improved tensile properties (PE3, PE4, PE7, PE10).
Degree of MMT platelets dispersion in composites was probed with X-ray diffraction. The results are presented in Fig. 2. All the curves exhibit a shoulder on the increasing slope at $2\theta = 2.0–2.9^\circ$. The curves for PE6, PE7, PE8 and PE9 samples have significantly lower shoulders. It indicates that the exfoliation of MMT platelets is rather high in those samples. For other samples the shoulder on the slope is much larger suggesting low penetration of compatibilizer and/or PE between MMT platelets and low level of exfoliation.

All samples were subjected to screening investigation of thermogravimetric properties. The exemplary curves for the samples PE1, PE7, PE8 and PE9 are plotted in Fig. 3. The onset temperatures of thermooxidative degradation (determined as the loss of 5% of weight of a sample) are varying largely and the highest onset temperature is for sample PE7 (LDPE-80 wt.%, Fusabond EMB 226D-15 wt.% and Cloisite 15A-5 wt.%) which is 62 °C higher than the onset temperature for pristine PE (PE1, 359.5 °C). Such large difference results from a significant reduction of oxygen penetration and a reduction of release of volatile degradation products in PE7 nanocomposite as compared to pristine LDPE (PE1). For other samples the increase in the degradation onset temperature is lower varying between 10 and 32 °C which may indicate lower degree of MMT exfoliation.

### 3.2. Influence of compounding conditions on structure and properties of nanocomposites

The aim of this part of work was to study the influence of the compounding parameters and variations in extruder configuration on the structure and properties of nanocomposites. PE7 composition (LDPE-80 wt.%, Fusabond EMB 226D-15 wt.%, Cloisite 15A-5 wt.%) was chosen for further studies because the preliminary investigations showed that PE7 nanocomposite shows the best mechanical properties, highest temperature of the onset of thermooxidation and also X-ray diffraction indicates the best exfoliation of MMT among other composites tested.

Two temperature profiles of the twin screw extruder were used ($T_1 = 150, 160, 170, 170, 170$; and $T_2 = 170, 180, 190, 190, 190^\circ C$), two screw speeds $N_1 = 250, N_2 = 400$ min$^{-1}$, and two screw configurations: $K_2$ described previously in [22] and $K_3$ presented in Fig. 1. Configuration $K_3$ consists one more set of shearing elements than configuration $K_2$. The
additional shearing elements are placed immediately before the first degasing zone. Right before additional shearing elements there is a back-pumping segment. All these causes that the composite is subjected to stronger shear in configuration $K_3$ than in configuration $K_2$. Sample codes and compounding condition of the samples prepared are listed in Table 3.

Fig. 2. 2θ X-ray diffraction curves of powdered nanocomposites from PE4 to PE12. Curves are shifted in the vertical direction to visualize better the changes.

Fig. 3. The loss of mass plotted against the temperature for samples PE1, PE7, PE8 and PE9. Heating rate 20 °C/min in air.
Tensile mechanical properties data of the nanocomposites from PE13 to PE15a are also reported in Table 3. Analysis of the data from the table leads to the following statements:

- Samples prepared applying the temperature profile \( T_2 \) (temperatures higher by 20°C in each heating zone of the extruder than for the \( T_1 \) profile) are characterized by lower MFR values and better mechanical properties (higher tensile strength, higher strain at fracture and higher tensile modulus).

- All sample prepared while applying the temperature profile \( T_2 \) show similar mechanical properties (tensile strength, strain at fracture and tensile modulus), the differences do not exceed 10%.

- For samples prepared applying the same temperature profile better properties are for lower screw speed, for example the samples prepared applying temperature profile \( T_2 \) and lower screw speed \( N_1 \) show the best mechanical properties and lowest MFR (samples PE13a and PE15a).

- For samples prepared with the same temperature profile and the same screw speed the screw configuration has little effect on the properties – the differences are less than few percent (compare samples PE13a and PE15a with PE14a and PE16a, respectively).

The exfoliation of the samples from PE13 to PE15a was studied by X-ray diffraction. The respective diffraction profiles are presented in Fig. 4. The

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Temp. profile ( ^\circ\text{C} )</th>
<th>Screw configuration</th>
<th>Screw speed ( \text{min}^{-1} )</th>
<th>MFR ( \text{g/10 min, 190}^\circ\text{C,2.16 kg} )</th>
<th>Tensile strength ( \text{MPa} )</th>
<th>Stress at fracture ( \text{MPa} )</th>
<th>Strain at fracture ( % )</th>
<th>Elastic modulus ( \text{MPa} )</th>
</tr>
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<tbody>
<tr>
<td>PE13</td>
<td>( T_1 )</td>
<td>( K_2 )</td>
<td>( N_1 )</td>
<td>0.53</td>
<td>19.7</td>
<td>18.0</td>
<td>108</td>
<td>349</td>
</tr>
<tr>
<td>PE14</td>
<td>( T_1 )</td>
<td>( K_2 )</td>
<td>( N_2 )</td>
<td>0.58</td>
<td>19.0</td>
<td>17.3</td>
<td>110</td>
<td>342</td>
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<tr>
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<td>( K_3 )</td>
<td>( N_1 )</td>
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<td>18.5</td>
<td>17.0</td>
<td>122</td>
<td>312</td>
</tr>
<tr>
<td>PE16</td>
<td>( T_1 )</td>
<td>( K_3 )</td>
<td>( N_2 )</td>
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<td>18.5</td>
<td>16.3</td>
<td>126</td>
<td>322</td>
</tr>
<tr>
<td>PE15a</td>
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<td>( N_1 )</td>
<td>0.47</td>
<td>22.3</td>
<td>20.4</td>
<td>132</td>
<td>369</td>
</tr>
<tr>
<td>PE14a</td>
<td>( T_2 )</td>
<td>( K_2 )</td>
<td>( N_2 )</td>
<td>0.59</td>
<td>21.0</td>
<td>19.1</td>
<td>139</td>
<td>344</td>
</tr>
<tr>
<td>PE15a</td>
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<td>( N_1 )</td>
<td>0.45</td>
<td>22.7</td>
<td>20.8</td>
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<tr>
<td>PE16a</td>
<td>( T_2 )</td>
<td>( K_3 )</td>
<td>( N_2 )</td>
<td>0.49</td>
<td>21.3</td>
<td>19.7</td>
<td>152</td>
<td>356</td>
</tr>
</tbody>
</table>

Fig. 4. X-ray diffraction profiles of the samples compounded according to protocols as presented in Table 4 (samples from PE13 to PE15 and from PE13a to PE15a). Curves are shifted vertically for better visualization of the changes in diffraction.
X-ray diffraction curves in Fig. 4 do not show any shoulder on the increasing slope, except for the sample PE15. The general conclusion at this point is that changing the compounding protocol one may achieve significant improvement in the exfoliation of MMT. The counterpart of sample 15, which is sample PE15a, prepared with the same screw configuration K3, same screw rotation speed N1 but at a different temperature profile T2, instead of T1, exhibits the highest degree of exfoliation with a smooth X-ray diffraction curve.

The samples from PE13 to PE15a were subjected to screening investigation of thermogravimetric properties. For this set of sample the onset temperature of thermooxidative degradation are varied within 13 °C range only. However, the samples PE13, PE14 and PE15, compounded at the lower temperature profile T1, are characterized by lower onset temperatures of thermooxidative degradation than the respective samples PE13a, PE14a and PE15a, the highest being for the sample PE15a. These results are in a good correlation with mechanical properties and MFR data from Table 3: highest thermooxidation resistivity for the sample PE15a coincides with its best mechanical properties and lowest melt flow index.

The melting and crystallization of the samples from Table 4 indicate that the melting temperature and degree of crystallinity do not depend significantly on the compounding protocol: melting temperature being similar as for pristine PE at around 112–113 °C, while the degree of crystallinity slightly higher at 48–50 wt.% of PE component in the nanocomposite than in pristine PE 46 wt.%.

### 3.3. Processing LDPE nanocomposites by film blowing

For further study of film forming we chose three materials: PE15a as the best nanocomposite which we were able to develop, PE15 – its counterpart obtained applying the lower temperature profile T1 and pristine LDPE MALEN E GGNX 23D022 (PE1). As the method of processing a film blowing was used as it is most commonly used in industry.

The following blown films were prepared: FPE01.I films from pristine LDPE FABS 23D022, FPE15.I films prepared from nanocomposite PE15 and FPE15a.I films from nanocomposite PE15a. The symbol I assumes the value of the applied film blow ratio: 3 or 6. The films were subjected to exhausting investigations typical for packaging films including: tensile properties, tearing resistance, oxygen permeativity, free surface energy, degree of crystallinity, atomic force microscopy and MMT platelets orientation by FTIR spectroscopy.

Mechanical properties of the films are presented in Table 4 for blowing ratios of 3:1 and 6:1, respectively. The film thickness in each case was 0.022 ± 0.002 mm in spite of different blow ratios due to setting a different extruder screw rotation speed: 30 min⁻¹ for blow ratio 3:1 and 45 min⁻¹ for blow ratio of 6:1.

The data analysis leads to the conclusion that independently of the blow ratio all films from nanocomposites exhibit worse mechanical properties in both directions than the film from a pristine LDPE. Films obtained with lower blow ratio show lower tensile properties in the transverse direction, while with higher blow ratio lower tensile properties are in the longitudinal direction. However, independently of the blow ratio the tearing resistance is higher for all films prepared from nanocomposites.

The results of measurements of oxygen permeativity are collected in Table 5. Oxygen permeativity of the films depends significantly on the blow ratio and is lower for higher blow ratio. The lowest oxygen permeativity has the film prepared with the high blow ratio 6:1 and from the nanocomposite PE15a.

#### Table 4

The results of mechanical properties investigation of blown films of pristine LDPE and nanocomposites in longitudinal and transverse directions with respect to sleeve take-up direction

<table>
<thead>
<tr>
<th>Film codes</th>
<th>Tensile strength (MPa)</th>
<th>Stress at fracture (MPa)</th>
<th>Strain at fracture (%)</th>
<th>Tearing resistance (N)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Longitudinal</td>
<td>Transverse</td>
<td>Longitudinal</td>
<td>Transverse</td>
</tr>
<tr>
<td>FPE01.3</td>
<td>30.4</td>
<td>18.3</td>
<td>28.4</td>
<td>17.8</td>
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<tr>
<td>FPE15.3</td>
<td>25.9</td>
<td>17.5</td>
<td>23.4</td>
<td>16.3</td>
</tr>
<tr>
<td>FPE15a.3</td>
<td>29.0</td>
<td>14.2</td>
<td>25.1</td>
<td>11.4</td>
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<td>FPE01.6</td>
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<td>28.1</td>
<td>19.4</td>
<td>27.1</td>
</tr>
<tr>
<td>FPE15.6</td>
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<td>22.4</td>
<td>16.8</td>
<td>18.5</td>
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<tr>
<td>FPE15a.6</td>
<td>19.8</td>
<td>21.4</td>
<td>11.9</td>
<td>15.9</td>
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</tbody>
</table>
The permeativity of this film is 40% less than the permeativity of a film from pristine LDPE and also 30% less than a similar film prepared from the nano-composite PE15. It means that the permeativity is a direct function of the exfoliation degree.

The melting temperature and the degree of crystallinity for the blown films were determined based on DSC measurements. The data are in Table 5. As it is seen from the table different blow ratios and addition of differently exfoliated MMT do not influence markedly the film melting temperature and the polyethylene crystallinity in nanocomposite films. Also the free surface energy is not influenced in a significant way either by blowing or by incorporation of MMT, and it is similar to the free surface energy of pristine LDPE given in the literature 35.7 mJ/m² [25].

The supermolecular structure of blown films was studied by means of atomic force microscopy in a tapping mode. The exemplary AFM images are presented in Fig. 5. Spherulitic aggregates were not detected either on inner or outer surface of the films. The main feature seen on surfaces of all films are crystals that are elongated, narrow and thin, the thickness being in the range of 10–12 nm. The shape of crystals is ribbon-like rather than lamellar. One can hardly distinguish stacks of crystals. The above observation agrees with earlier results concerning ribbon-like crystals of low density polyethylene [26–31]. Similar results were also obtained by others using AFM [32–37], except that in some cases, when the blow ratio was low, spherulitic morphology was observed (e.g. [33]). The structure of ribbon-like crystals is similar to polymer lamellar crystals with chain folding except that their width is reduced nearly to their thickness. Only on the surface of FPE01.3 film a shish-kebab structure can be distinguished (note the elongated structure on the right side in Fig. 5a), other crystals seem to have similar chain packing as in un-oriented LDPE films. It should be noticed that on AFM images of the surface of FPE15a.6 there are often seen platelets of MMT (see Fig. 5c). All of them are exfoliated and separated from MMT stacks which confirm the conclusion based on X-ray diffraction (see Fig. 4) of full exfoliation of nanocomposite PE15a. The crystalline structure seen on surfaces of films from pristine LDPE (FPE01.3 and FPE01.6 (Fig. 5a and b) does not differ significantly from the respective crystalline structure of LDPE in nanocomposite (FPE15a.6, Fig. 5c).

The crystal orientation of blown films was probed by X-ray pole figure analysis and SAXS. The data are presented in Fig. 6. From the pole figures it is possible to deduce the preferential orientation directions of crystallographic planes while from SAXS the information on crystal packing is obtained. Both combined information should be sufficient for the description of the texture of films. In the film prepared from pristine LDPE with the blow ratio 3:1 there are two populations of PE crystals: first is oriented with (020) planes parallel to the film surface and second with (200) planes distributed widely over large range of beta angles (see Fig. 6a). The first population of crystals gives a faint diffused ring in the SAXS pattern. It is evident from AFM images (Fig. 5) that the ribbon-like crystals do not form very regular stacking, however, the crystal-amorphous packing shows some periodicity. The long period calculated from a weak diffused ring is then 10.1 nm.

The second population of crystals is tilted at some acute angle with respect to the take-up longitudinal direction and having the (020) planes at some acute angles (30–60°) with respect to the film surface (see Fig. 6a). The (200) planes of those ribbon-like crystals are tilted 20–30° away from the equator of the pole figure (Fig. 6a) towards

<table>
<thead>
<tr>
<th>Sample codes</th>
<th>Mean film thickness (µm)</th>
<th>Oxygen permeativity (cm³ mm/m² 24 h atm)</th>
<th>Degree of crystallinity (%)</th>
<th>Melting temperature (°C)</th>
<th>Free surface energy (mJ/m²)</th>
<th>Long period along take-up direction (nm)</th>
<th>Long period along blow direction (nm)</th>
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<tr>
<td>FPE01.3</td>
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<td>386</td>
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<td>264</td>
<td>48.4</td>
<td>114.40</td>
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<td>114.48</td>
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<td>216</td>
<td>47.1</td>
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<td>36.7</td>
<td>11.0</td>
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<tr>
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<td>190</td>
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<tr>
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<td>114.47</td>
<td>36.3</td>
<td>10.8</td>
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</tr>
</tbody>
</table>
take-up direction. That population of crystals give rise to a faint two-point SAXS pattern for the film if illuminated perpendicularly to its surface. However, most of those crystals should scatter X-ray
Fig. 6. (a)-(f) Pole figures and SAXS patterns for blown films. Film codes are placed on the figures. Vertical direction is the take-up direction while horizontal direction is the blowing direction. In (a) two other SAXS patterns are shown for the sample tilted around take-up axis by 25° and 45°.
when the sample is turned around the take-up axis by 25° and further by 45° (oblique X-ray illumination). Then more crystals with adjacent amorphous layers are oriented according to Bragg condition and the two-point SAXS pattern becomes more intense (see Fig. 6a). The long period calculated from two-point SAXS pattern is then 10.8 nm.

As the blow ratio is increased to 6:1 (see Fig. 6b) the first population of lamellae is increased giving a strong diffused ring in SAXS pattern. The second population of crystals is now low and reflected in a weaker intensity of two-point SAXS pattern and in a diffused population of (020) planes in the equatorial position over the 2θ range from 30° to 80° in the respective (020) pole figure. For both blow ratios 3:1 and 6:1 the concentration of normals to (110) planes in the pole figures confirm the above conclusions.

The introduction of MMT into the films blown with the ratio of 3:1 makes the texture less pronounced: the first population of ribbon-like crystals, quite large in pristine 3:1 blown film, is nearly gone in FPE15a3 nanocomposite film. The clustering of (200) normals in polar regions of the respective pole figure (Fig. 6c) is less intense than on a similar pole figure for 3:1 blown pristine LDPE film (sample FPE01.3, in Fig. 6a) and limited to lower 2θ angles. The long period as calculated from the two-point SAXS pattern is larger at 11.2 nm which apparently results from a larger tilt angle of majority of ribbon-like crystals with respect to the film surface and not because there was a change in crystallinity.

When blowing the nanocomposite film with higher blow ratio 6:1 the texture sharpens (Fig. 6d). The texture of LDPE crystals is now similar to the texture of pristine LDPE film blown with the ratio of 6:1, also for the second population of ribbon-like crystals that nearly disappeared. As the result we do not observe the two-point SAXS pattern and only a diffused ring. The long period calculated is nearly 11 nm in both take-up and blowing directions.

The texture of the film blown from nanocomposite PE15a with the blow ratio of 3:1 is very similar to the texture of pristine LDPE blown to the same ratio 3:1, except for the lower first population of crystals with (200) planes perpendicular to the film surface (Fig. 6e). Also the SAXS pattern is very similar, however, a diffused ring, connected with the first population of crystals in the FPE01.3 film, here is absent.

Blowing the film of PE15a nanocomposite to the ratio 6:1 generates larger amount of crystals belonging to the first population, as it is seen from pole figures in Fig. 6f. The two-point SAXS pattern is now supplemented with a diffused ring characteristic for the first population of crystals. In all above cases the
long period is not significantly altered, as it is seen from Table 5.

The general conclusion from the above study of texture is that the two texture components are: the first connected with the formation of a free surface of films and the second connected with molecular orientation due to blowing and take-up rate ratio (8:1). Similar conclusion concerning dual texture of pure un-filled high density PE blown films were drawn by others [38,39], however, in contrast to our LDPE blown films those HDPE texture components were connected with lamellar stacks in machine and transverse orientation directions due to blowing and not to the formation of a free surface of the film. Further observations shows that in the film FPE01.3 the structures that can be identified as shish-kebab are occasionally identified.

The presence of nanoclay in films decreases significantly the sharpness of texture of crystalline part of LDPE. In addition, the crystallinity degree of polyethylene component and long period determined from SAXS were nearly independent of the additives, which means that the compatibilizer (Fusabond EMB 226D) is located preferentially around nanoclay platelets and is not entering to the amorphous layers of LDPE.

The orientation of clay platelets was probed by means of FTIR. We followed the techniques developed by Cole and others [40,41]. It relays on recording of three IR spectra: SM, ST and SN SF and an exemplary subtracted SN-f*SF are presented for the polyethylene nanocomposite film FPE15.3.

The obtained Hermans orientation factors for the blown films are +0.61, +0.64, +0.66 and +0.68 for FPE15.3, FPE15.6, FPE15a.3 and FPE15a.6 films, respectively. The values are between 0.61 for the nanocomposite FPE15.3 film with the blow ratio of 3:1 and 0.68 for nanocomposite film FPE15a.6 with the blow ratio 6:1. Those values indicate some orientation of platelets but rather far from a perfect one for which the Hermans orientation factor should be 1.0. In the paper by Cole, Perrin-Sarazin and Dorval-Douville [41] the Hermans orientation factor was at the level of 0.74–0.80 for blown films of polypropylene nanocomposite. However, the take-up ratio in Cole et al. experiments was 24 while in our case it was only 8. Those, rather low, Hermans orientation factors correlate well with the measured oxygen permeativity in Table 5. The correlation confirms that the controlling process for permeativity is a significant increase in a diffusion path.
because gas molecules cannot permeate through MMT platelets.

4. Conclusions

1. The results of compounding of nanocomposites indicate a significant role of a type of montmorillonite and a type of a compatibilizer for the properties of polyethylene based nanocomposites. A nanocomposite with MMT having larger gallery distance \( d_{001} = 3.15 \text{ nm} \) and with a compatibilizer of low melt flow index (MFR = 1.5 g/10 min) being close to the melt flow index of base polymer are characterized by better exfoliation and better mechanical and thermal properties.

2. Nanocomposite processed at higher temperatures of all extruder zones (temperature profile \( T_2 \)) and at lower screw rotation speed \( (N_1 = 250 \text{ min}^{-1}) \) shows the best mechanical properties and best thermal stability – its degradation onset is 90 °C higher than the onset temperature of pristine polyethylene. Such improvement in thermal stability evidences a high degree of MMT exfoliation. Those results are in agreement with earlier observations that the longer residence time in the extruder (lower screw rotation speed) and higher temperature are preferred for enabling the diffusion of polymer chains into the galleries. The small difference in nanocomposite properties if two different screw configurations are applied results probably from the fact that both configurations (K2 and K3) consist kneading elements which are sufficient for de-agglomeration of MMT particles.

3. Blown film properties depend very much on the nanocomposite used and also on the blowing process parameters. Films blown with higher blowing ratio are characterized by slightly worse mechanical properties but have improved barrier properties as compared to films from pristine polyethylene and to films blown at lower blow ratio. Films exhibit similar crystallinity of polyethylene component independent of the blow ratio. The long period characteristic for polyethylene component is also not drastically altered. From the independence of the long period (by SAXS) and of the crystallinity of LDPE component in nanocomposites it follows that the compatibilizer (Fusabond EMB 226D) is located preferentially around nanoclay platelets and is not entering to the amorphous layers of LDPE. The texture of blown films consists of two texture components connected: the first with the formation of a free surface of films and the
second with molecular orientation due to blowing ratio (3:1 or 6:1) and take-up rate ratio (8:1). The presence of nanoclay in films decreases significantly the sharpness of the texture of crystalline part of LDPE.

4. Oxygen permeativity of blown films depends clearly on the orientation of clay platelets and the degree of their dispersion. Higher blow ratio and better exfoliation clearly cause a decrease of permeativity of films. These findings support undoubtedly the concept of a significant increase in a diffusion path in films with better exfoliation of MMT and stronger orientation of platelets, parallel to the film surface. Applied take-up ratio and blow ratio limit the suppression of oxygen permeation, however, for the best nanocomposite film (FPE15a.6) the oxygen permeativity is reduced 2.5 times in comparison to pristine LDPE film (FPE01.3).

5. A kind of nanocomposite and processing conditions have little effect on the free surface energy. Apparently all the films require surface modification before printing, painting or laminating.

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References


