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Polyethylene and Poly(propylene)/Clay Nanocomposites

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Polyethylene and polypropylene nanocomposites were investigated with focus on mechanical and barrier properties. Structure was observed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Four types of nano-filler were used: Nanofil 5, 8, 9 and 3000. In case of polyethylene nanocomposites the dispersion and intercalation was to low extent. Mechanical and barrier properties were worse compared to pure PE. In case of polypropylene with Nanofil 5, 9 and 3000 tensile strength was better compared to pure PP. Also PP with Nanofil 9 and 3000 had better barrier properties than pure PP for both O_2 and CO_2. This was explained by better intercalation and dispersion of the filler documented by XRD measurement and TEM observation.

Keywords: mechanical and barrier properties; morphology; nanocomposites; polyolefin

Introduction

Nanocomposites represent a group of materials which has been studied since 1990s. The nanocomposite consists of two chemically different materials: polymer matrix and nanofiller. For example polypropylene, polyethylene, polystyrene were used as polymer matrix.[1–5] Examples of nanofillers are clay minerals, especially montmorillonite. Vermiculite and sepiolite are the other types of clay minerals used as nanofillers.[6–10]

The proper preparation of polyolefin nanocomposites is extremly difficult. The reason behind that is different polarity between polyolefin and natural clay mineral. One possible solution to overcome this problem is a modification of clay minerals and the use of a suitable compounding device.

The modification of clay minerals can be performed by ion exchange or ion dipole method. Figure 1 shows the principle of both mentioned methods.

The ion dipole method is the first type of modification. Ion dipole method can be performed in liquid or in melt and this method is called ‘‘dry way’’. Ion exchange method is the second type of modification. Ion exchange method proceeds in liquid state thus it is called ‘‘wet way’’. The secondary product (Na^+) is washed away. Ion dipole method is easier than ion exchange method because it is not necessary to wash away the secondary product.

The type of compounding device can influence the level of intercalation and/or exfoliation of a filler and final properties of prepared nanocomposites. A single screw extruder, twin screw extruder or kneader are devices that can be used for compounding.[11]

The motivations for the research of nanocomposites are quite unique properties in comparison with pure polymer matrix. The presence of a clay mineral causes higher tensile strength, modulus, better barrier properties and lower flammability of nanocomposites.[12–19]

This study reports the comparative study on polyethylene and polypropylene/clay nanocomposites. Nanocomposites were prepared by the same compounding device at various preparation conditions. The morphology was evaluated by X-ray diffraction (XRD) and by transmission electron microscopy (TEM). Changes of barrier and mechanical properties were observed too.

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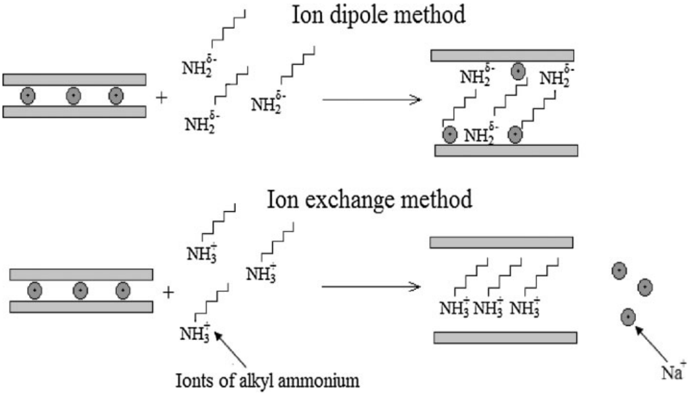

Figure 1.
Methods of modification of clay minerals.

Experimental Part

Materials

Five different materials were used in this work. Polymer matrixes consisted of two polyolefinic polymers: polyethylene and polypropylene. Polyethylene DOWLEX 2035 E and maleated polyethylene were supplied by Dow Chemicals.

Polypropylene Mosten GB 003 was produced and supplied by Chemopetrol Litvinov, Czech Republic. Maleated polypropylene Exxelor 1015 was supplied by ExxonMobil Chemical Europe, Belgium. The maleated polymers were added in concentration 5 wt. %. Table 1 shows density and melt flow indexes of polymer materials used in this study.

Series of commercial fillers Nanofil (types Nanofil 5, Nanofil 8, Nanofil 9 and Nanofil 3000) were used as nanofillers. The producer of Nanofil is Südchemie, Germany. Concentration of all fillers was 3 and 5 wt. %. The specification of fillers is shown in Table 2.

Preparation of Polyolefin/Clay Films

Polyolefin/clay films were prepared in two steps. The first step was preparation of pellets. Pellets were prepared by use of single screw extruder KO BUSS. The line used for preparation of pellets consisted of a single screw extruder, water bath and a pelletizing device. Preparation conditions were varied for different polymer materials. Table 3 shows the preparation conditions for both types of polymer materials.

Prepared pellets were used in the following step: preparation of polyolefin/clay films. The line was consisted of a single screw extruder Brabender PL 2000 with a flat die, chilled calender and a winding machine. The thickness of films was controlled by the speed of winding machine.

Table 1.
Polymer materials: density and melt flow indexes.

Polymer materials	Density [g/cm^3]	Melt flow index [g/10 min]
Polyethylene Dowlex 2035	0.919	6.00
Maleated polyethylene Amplify GR 216	0.916	1.25
Polypropylene Mosten GB 003	0.907	3.20
Maleated polypropylene Exxelor 1015	0.900	22.00

Table 2.
Specification of Nanofil fillers.

Type of filler	Modificator	clay spacing [nm]
Nanofil 5	Distearyldimethylamonium chloride	2.8
Nanofil 8	Distearyldimethylamonium chloride	3.5
Nanofil 9	Stearylbenzyldimethylamonium chloride	2.0
Nanofil 3000	Distearyldimethylamonium chloride	2.6

Table 3.
Preparation conditions for polyethylene and polypropylene/clay nanocomposites.

Preparation conditions	Polyethylene/clay nanocomposite	Polypropylene/clay nanocomposite
T_1 [°C]	110	155
T_2 [°C]	150	165
T_3 [°C]	160	170
T_4 [°C]	170	180
T_5 [°C]	190	–
T_6 [°C]	190	–
The screw speed [rpm]	67	65
The kneader speed [rpm]	280	270

Table 4 shows the conditions of film preparation. The thickness of PE/clay films was in the range of 0.11–0.13 mm and PP/clay films was 0.12–0.13 mm.

Technique Used for Evaluation of Polyolefin/Clay Nanocomposites

The morphology of prepared polyolefin/clay nanocomposites was evaluated by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

Specimens for X-ray diffraction were prepared by compression moulding. The temperature for moulding of PE/clay desk was 180 °C, time of moulding was 9 min and time of cooling was 12 min. The temperature for moulding of PP/clay nanocomposites was 220 °C. Time of moulding was 9 min and time of cooling was 12 min. X-ray diffraction was measured by using diffractometer URD. Conditions of measurement were following: reflex mode, angle 2θ was 2–30°, step 0.05.

Table 4.
Conditions for production of polyolefin/clay films.

Conditions of preparation	Polyethylene/clay nanocomposite	Polypropylene/clay nanocomposite
T_1 [°C]	110	150
T_2 [°C]	150	210
T_3 [°C]	160	230
T_4 [°C]	170	230
T_5 [°C]	190	230
T_6 [°C]	190	230
The screw speed [rpm]	40	35
The winding speed [rpm]	5	6

The structure was observed directly by transmission electron microscopy (TEM). Ultra thin sections were cut with an ultracryomicrotome LEICA ULTRACUT UCT at −110 °C. TEM pictures were taken on JEM 200CX (JOEL) at 100 kV. Obtained pictures were digitalized by using digital camera DXM1200 Nikon which was controlled by a computer.

Mechanical properties (tensile strength and elongation at break) were tested by tensile test machine T 200, Alpha Technologies. Conditions were following: the moving clamp distance was 60 mm and the rate was 25 mm/min for all specimens.

Injection moulding was also used for sample preparation. The injection moulding device DEMAG NC4 was used only for preparation of PP/clay specimens. Zone temperatures were following: 80 °C, 190 °C, 210 °C, 230 °C and 240 °C. The cycle time was 30 seconds.

PE/clay specimens were prepared by compression moulding. The temperature of the mould was 180 °C, time of moulding was 9 min and time of cooling was 12 min.

Barrier properties were measured according to the standard CSN 64 0115-B. Polyolefin/clay films were used as specimens. Device LMP 150 was used as a measuring device from TESLA Roznov p. Radhostem, Czech Republic. Conditions were following:

the temperature was 25 °C; humidity was 48% and the time of measuring was 48 hours.

Results and Discussion

Morphology of Polyethylene/Clay Nanocomposites

X-ray diffraction and TEM were used for morphology evaluation of prepared nanocomposites.

Figure 2 shows PE nanocomposites filled with Nanofil 8. The concentration of filler was 3 and 5 wt. %. In case of XRD measurement there is possible to see peaks belonging to a nanofiller. The 2 θ angle range was found to be 5–8. The TEM pictures revealed the presence of agglomerates.

Figure 3 shows TEM picture of polyethylene/Nanofil 8 sample. There are agglomerates of filler in the matrix. Agglomerates of fillers had size larger than 500 μm. Figure 3 also shows that the distribution and dispersion of the filler are rather poor.

Mechanical Properties of Polypropylene/ Clay Nanocomposites

Tensile strength and elongation at break are important mechanical properties and therefore they were measured. Data are shown in Table 5. Figure 4 presents data of tensile strength.

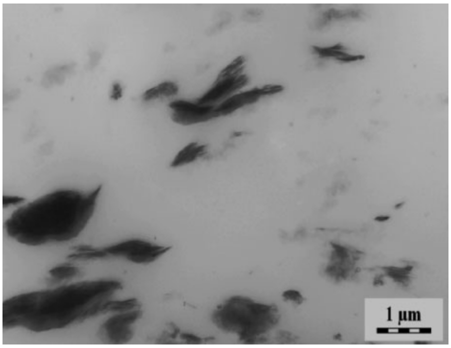

Figure 3.
TEM picture of polyethylene containing 5 wt. % of Nanofil 8.

As can be seen from the data in Table 5, the maximum value of tensile strength for specimens containing 3 wt. % of filler is lower than the value of the virgin polyethylene. The minimum was obtained for filler Nanofil 8 and the value is only ¼ of the tensile strength of pure polyethylene.

The similar situation was for specimens filled with 5 wt. % of nanofiller. The maximum was obtained for PE/Nanofil 5. However, the top of tensile strength is higher only about a 0.26 MPa in comparison

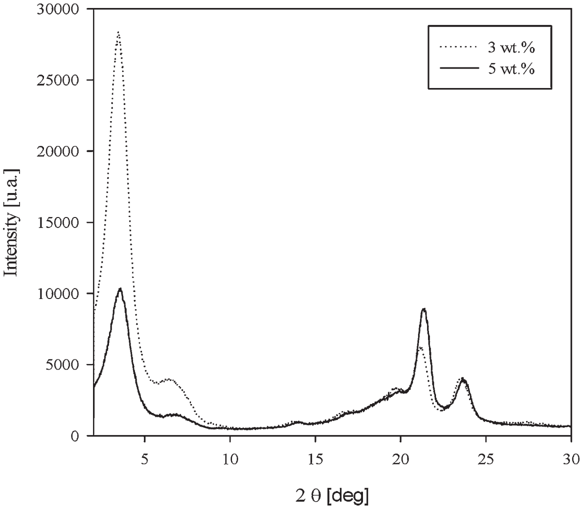

Figure 2.
XRD results of polyethylene nanocomposites filled with 3 and 5 wt. % of Nanofil 8.

Table 5.
Tensile strength and elongation at break of polyethylene/clay nanocomposites.

	Tensile strength [MPa]		Elongation at break [%]	
	3 wt. %	5 wt. %	3 wt. %	5 wt. %
The pure PE	14.72	14.72	86.60	86.60
Nanofil 5	14.19	14.98	35.70	36.17
Nanofil 8	3.39	2.89	9.82	9.55
Nanofil 9	14.29	13.94	24.05	23.61
Nanofil 3000	12.46	11.22	19.54	21.11

with the pure polyethylene. Other values of tensile strength are lower than for the pure polyethylene matrix. The same situation is for the lowest value of tensile strength. The minimum was measured for polyethylene matrix containing 5 wt. % of Nanofil 8.

Elongation at break data of showed that all prepared nanocomposites had lower elongation at break which can be explained by the presence of agglomerates of the filler. The maximum was measured for PP filled with 5 wt% of Nanofil 5 and the minimum for specimen containing 5 wt% of Nanofil 8.

Barrier Properties of Polyethylene/Clay Nanocomposites

Barrier properties are very important for application of polymers in packaging. The results of permeability of O_2 and CO_2 are shown in Table 6.

Data show that the permeability of prepared nanocomposites is higher than the pure polyethylene. However, polyethylene filled with 3 wt. % Nanofil 5 had lower permeability of CO_2 but the value is not relevant because the situation is dissimilar for O_2.

Mechanical and barrier properties were influenced by intercalation of the fillers. Next evaluated nanocomposites were polypropylene/clay.

Morphology of Polypropylene/Clay Nanocomposites

The situation was different in case of polypropylene/clay nanocomposites. Figure 5 shows X-ray pattern of polypropylene containing both concentration of Nanofil 8. X-ray pattern shows peaks of agglomerates; however, the degree of intercalation is better. The intercalation was better for polypropylene filled with 3 wt. % of Nanofil 8. The XRD results were supported by TEM pictures.

Figure 6 shows TEM picture of polypropylene filled with 5 wt. % of Nanofil 8. As can be seen in Figure 5, the intercalation of the filler was better in comparison with polyethylene nanocomposite. Distribution

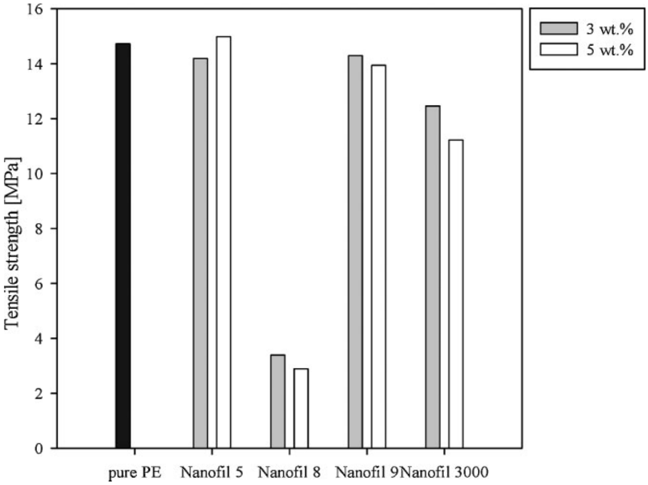

Figure 4.
Tensile strength of PE/clay nanocomposites.

Table 6.
Barrier properties of PE/clay nanocomposites.

	Q_{O2} [$m^2.Pa^{-1}.s^{-1}$]		Q_{CO2} [$m^2.Pa^{-1}.s^{-1}$]	
	3 wt. %	5 wt. %	3 wt. %	5 wt. %
The virgin PE	$2.97\ 10^{-17}$	$2.97\ 10^{-17}$	$9.39\ 10^{-17}$	$9.39\ 10^{-17}$
Nanofil 5	$5.21\ 10^{-17}$	$8.31\ 10^{-17}$	$1.48\ 10^{-17}$	$2.23\ 10^{-16}$
Nanofil 8	$5.11\ 10^{-17}$	$5.81\ 10^{-17}$	$1.10\ 10^{-16}$	$1.42\ 10^{-16}$
Nanofil 9	$8.81\ 10^{-17}$	$6.82\ 10^{-17}$	$1.71\ 10^{-16}$	$2.69\ 10^{-16}$
Nanofil 3000	$7.72\ 10^{-17}$	$8.75\ 10^{-17}$	$1.68\ 10^{-16}$	$2.58\ 10^{-16}$

of filler is regular and dispersion of filler is at higher level in comparison with PE/clay nanocomposite. The thickness is from 100 to 300 nm. However, we can see that polypropylene/clay nanocomposites contained some agglomerate too.

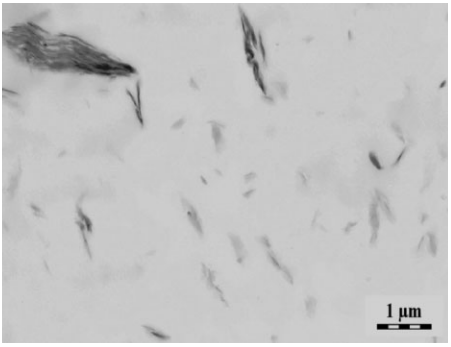

Figure 6.
TEM picture of PP/Nanofil 8 (5 wt. %) nanocomposites.

Mechanical Properties of Polypropylene/Clay Nanocomposites

Table 7 shows the results of tensile strength and elongation at break of polypropylene/clay nanocomposite. Concerning polypropylene filled with 3 wt. % of the filler the lowest value was found for Nanofil 8 while the highest value was found for Nanofil 5. Composites containing Nanofil 5, 9 and 3000 had higher tensile strength than the pure PP. Concerning nanocomposites filled with 5 wt. % of the filler the highest value of tensile strength was found for Nanofil 3000, and the lowest value was found for Nanofil 8.

Results from measurement of elongation at break showed lower values compared to the pure PP. Lower elongation was probably caused by the presence of agglomerates of the nanofiller. The maximum was found for PP filled with 5 wt. % of Nanofil 3000 and the minimum for specimen containing 5 wt. % of Nanofil 8.

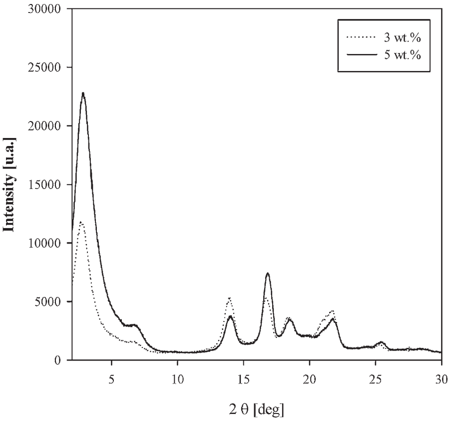

Figure 5.
X-ray pattern of polypropylene filled with 3 and 5 wt. % Nanofil 8.

Barrier Properties of Polypropylene/Clay Nanocomposites

Barrier properties data of the polypropylene/clay nanocomposites are shown in Table 8.

Table 7.
Tensile strength and elongation at break for polypropylene/clay nanocomposites.

	Tensile strength [MPa]		Elongation at break [%]	
	3 wt. %	5 wt. %	3 wt. %	5 wt. %
The pure PP	14.10	14.10	98.32	98.32
Nanofil 5	25.16	21.28	37.89	40.02
Nanofil 8	7.33	8.62	16.93	16.61
Nanofil 9	20.98	25.56	37.03	45.81
Nanofil 3000	21.00	26.08	33.06	46.93

Table 8.
Barrier properties of polypropylene/clay nanocomposites.

	Q_{O2} [m^2.Pa^{-1}.s^{-1}]		Q_{CO2} [m^2.Pa^{-1}.s^{-1}]	
	3 wt. %	5 wt. %	3 wt. %	5 wt. %
The pure PP	2.09 10^{-17}	2.09 10^{-17}	3.30 10^{-17}	3.30 10^{-17}
Nanofil 5	3.01 10^{-17}	4.39 10^{-17}	4.28 10^{-17}	3.55 10^{-17}
Nanofil 8	3.76 10^{-17}	3.14 10^{-17}	4.77 10^{-17}	4.71 10^{-17}
Nanofil 9	1.89 10^{-17}	1.67 10^{-17}	2.15 10^{-17}	2.66 10^{-17}
Nanofil 3000	1.55 10^{-17}	1.88 10^{-17}	2.20 10^{-17}	2.78 10^{-17}

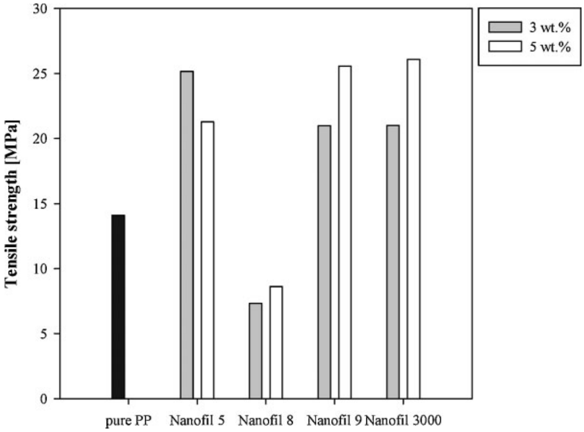

Figure 7.
Tensile strength and elongation at break of PP/clay nanocomposites.

Specimens filled with 3 and 5 wt. % of Nanofil 9 and Nanofil 3000 had lower permeability for both O_2 and CO_2 compared to pure PP. The remaining specimen had higher permeability in comparison with pure PP. Results are better compared to PE/clay nanocomposite when PE filled with Nanofil 9 and Nanofil 3000 had higher permeability for both types of gases.

Conclusion

In this study polyethylene and polypropylene nanocomposites were investigated. Nanocomposites were prepared on the identical device; however, the conditions were different for the specific materials. Properties of nanocomposites were compared with the pure polymers with focus on the morphology, tensile strength, elongation at break and barrier properties.

The morphology study (investigated by XRD and TEM) of polyethylene/clay nanocomposites revealed that the intercalation of the nanofillers was to somewhat lower extent. The distribution and dispersion of filler was quite poor too. The intercalation influenced the mechanical and barrier properties. Mechanical and barrier properties of the PE/clay nanocomposites were lower in comparison with the pure polyethylene. It is possible that selected fillers were not suitable for polyethylene matrix.

Different situation was observed for polypropylene/clay nanocomposites. The results from TEM picture showed regular distribution of a filler. The dispersion of filler Nanofil 8 was better, even though the specimen contained some agglomerates. The tensile strength was higher for all prepared nanocomposites with the exception of Nanofil 8 that had lower tensile strength. Data of elongation break was in accordance with the presence of agglomerates of nanofiller. The permeability of O_2 and CO_2 was lower for films filled with Nanofil 9 and Nanofil 3000.

In the future, other types of commercial fillers will be investigated for the same polymer materials. The different compounding devices will be used too.

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