The Effect of Low Temperature Air Plasma Treatment on Physico-chemical Properties of Kaolinite/Polyethylene Composites

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ABSTRACT

The effect of low temperature air plasma treatment on the physico-chemical properties of kaolinite/polyethylene composites was studied. Moreover, the kaolin powder was treated with (3-aminopropyl)triethoxysilane as a coupling agent to improve the interfacial adhesion between powder filler and polymer matrix. The modification of the kaolin resulted in a notable improvement in the mechanical strength and elastic modulus of filled polyethylene composites, compared to the virgin polymers. Observed improvement of the tensile strength became more marked as the filler loading increased, indicating an improved degree of filler/matrix interaction. Simultaneously the improvement of the fracture toughness of prepared HDPE and LLDPE kaolinite composites was confirmed. Moreover, the morphology of the grains distribution and tensile fracture surface was examined by electron microscopy confirming excellent distribution of the filler in the polymer matrix.

Keywords: *A. Polymer-matrix composites (PMCs); A. Particle-reinforcement; A. Thermoplastic resin; B. Fracture toughness; B. Plastic deformation; D. Mechanical testing; D. Thermal analysis*

1

Introduction

Characterization and modification of polymers are perhaps the most important aspects of polymer research, production and applications. Polyolefin polymers, especially thermoplastics have become an essential part of our everyday lives in the last few decades [1,2]. Thermoplastics, such as polyethylene (PE) can offer useful mechanical, chemical, electrical properties, with low density, high formability and the ability to be recycled. Due to its low price per unit volume and its unique physico-chemical properties it is therefore, the world's number one per volume most used thermoplastic [3,4]. This semi-crystalline polymer can be classified according its density and divided into four groups: high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), and very low density polyethylene (VLDPE) [5].

In the last few years, clay minerals were used as a cost reducer and as an additive triggering an improvement of the mechanical properties of polymer composites. Their surface modifications were used in catalysis, as an adsorbent, in sensors and as filler in polymer-clay composite systems [6]. The effect of incorporating inorganic fillers into the thermoplastic polymer network, results in the improvement of the physico-chemical and mechanical characteristics such as low air permeability, improved mechanical strength, modulus of elasticity and stiffness [7-11]. For this reason the research and development activities focused on composites containing inorganic filler is of expanding importance. Matrix modification, degree of crystallinity, type of reinforcement, quality of adhesion between filler and matrix, size, shape, size distribution of filler particles, addition of coupling agents affects the physico-chemical and thermo-mechanical properties, as well as internal structure and strength of aggregates [12-15]. In most cases, silane coupling agents are added to react with inorganic substrates in order to form stable covalent bonds, thus altering the physical interactions of treated polymer/filler substrates. As is very well known, polymer/kaolin interface quality performance is essential for excellent overall composite system material/mechanical properties, where exact adjustment of the polymer matrix modulus and adhesive bond strength is vital for final synergistic increase of mechanical strength of the composite system [16]. An effect of coupling agents on mechanical properties improvement of polymer/inorganic filler composites was studied and referenced in early works of Arkles *et al.* [17], Edwin. *et al.* [18] and Leyden. [19].

Kaolin is a clay mineral also known as China Clay or Paper Clay. The chief constituent of Kaolin (Al_2O_3 $2SiO_2$ H_2O), is kaolinite, which consists of successive layers of octahedral alumina and tetrahedral silica, which alternate to form plate like hexagonal particles. The particles are flat disks or plate like in shape, with the disk radius of the order 5-10 times larger than the thickness. Thus a typical crystal is a platelet of 0.5   1 microns in diameter and 0.1 microns thick. The flat surface is

2

negatively charged over the entire pH range, whilst the edges are positive at low pH, but negative at high pH, with an iso electric point at about pH 7. These edge effects arise due to the fracture of the lattice network and contain silica and alumina like sites [20, 21]. The electrokinetic behaviour of kaolinite should show an average of the surface and edge properties, but initial experiments revealed that the zeta potentials were negative over the entire pH range and were very similar to the silica zeta potential pH curve. This was explained by the large face to edge surface area ratio [20, 21]. Particle characterization of this clay mineral has previously been studied in our another paper by Lapcik *et al.* [20] and Greenwood *et al.*, [21].

The mechanical properties of particulate-polymer composites depend strongly on the particle size, particle matrix interface adhesion and particle loading [22, 23]. Polymer composites are noted to show mechanical properties which depend on time, deformation rate and temperature. However, the filler introduces a high amount of interface in the matrix that affects the polymer crystallization process and modifies the structure of the polymer in the neighborhood of the particle surface [22, 24].

The main aim of this paper was focused on studying the effect of low temperature air plasma treatment and silane coupling agent modification of nano/micro kaolinite filler particles on the physico-chemical, mechanical and thermal properties of polyethylene/kaolinite composite system with filler content ranging from 0 to 25 wt.%.

1   Materials

Two commercial polyethylenes were used in this study: HDPE TIPELIN 6300B and LLDPE LITEN, Unipetrol PND 33-300 (Czech Republic). As a virgin filler material kaolin (Imerys Minerals Ltd, Cornwall, UK) was used. For chemical modification of kaoline a silane coupling agent (3-aminopropyl)triethoxysilane (Sigma Aldrich, USA) was used.

3   Methods

3.1 Sample preparation

Air plasma treatment of the filler powder was performed in a Diener Femto (Diener Electronic, Germany) plasma reactor operating at 13.56 MHz frequency for 10 min., with generator power 100 W, air flow rate 5 cm^3/min and processing pressure 35 Pa. The polymers were filled with virgin and plasma treated kaolinite powder with the following content: 0, 2.5, 5, 7.5, 10, 15 and 25 wt %.
From a processing point of view, the important attitude was favourable dispersion of filler particles and minimizing their agglomeration. The latter agglomeration is probably due to the high surface energy of kaolin fillers [25]. Filled, homogenized polyethylenes were then injection-moulded in an

3

Arburg Allrounder 170 U 150-30 (Germany) machine in a form of a dogbone testing articles according to the CSN EN ISO294-1 and CSN ISO 293 standards. The processing parameters of the injection-moulding process used are shown in Table1.

Chemical modification of kaolin was realized using silane coupling agent (3-aminopropyl) triethoxysilane (Sigma Aldrich, USA) as a intercalation process supporter. The modification was performed with 3% vol. addition in 1:1 water-ethanol solution. Afterwards the substrate was stirred for 180 minutes by homogenizer at room temperature 24°C and then dried.

3.2 Tensile strength testing

Tensile strength measurements were performed with moulded dogbone testing articles (length of 75mm) using universal testing machine ZWICK 1456 (Germany). Measurements were performed at 50 and 200 mm/min deformation rates. Each measurement was repeated five times and mean average values were calculated. There were determined an ultimate tensile strength (F_{max}), elongation at break (ε) and elastic modulus (E) of a series of composites with varying filler content. Observed results are summarized in Tables 2-5.

3.3 Charpy V-notch impact test

The notched impact toughness was determined according to the TL 526 31 standard on Charpy´s hammer (0.4 kPm hammer) (CEAST Resil Impactor Junior, (Germany)) at 25 °C for each material under study. Each measurement was repeated five times. V-notched specimens were of the $5\times3\times58$ mm dimensions with notch depth of 2 mm.

3.4 Scanning Electron Microscopy

Scanning electron microscopy was used to follow fracture surface and filler particles morphology characteristics of the virgin and modified samples. Scanning electron microscopy (SEM) images were captured on a Hitachi 6600 FEG microscope (Japan) operating in the secondary electron mode and using an accelerating voltage of 1 kV.

3.5 Thermal Analysis

Thermo-gravimetry (TG) and differential thermal analysis (DTA) experiments were performed on simultaneous DTA-TG apparatus (Shimadzu DTG 60, Japan). Throughout the experiment, the sample temperature and weight-heat flow changes were continuously monitored.

Conditions of measurement: Heat flow 10°C/min and dynamic atmosphere of nitrogen (N_2 – 50 ml/min), range of temperature measurement was from 40 °C to 500 °C.

4   Results and Discussion

Figure 1 shows results of the tensile strength measurements for virgin and chemically modified plasma treated filler particles composites with HDPE. It is evident, that the highest increase in ultimate tensile strength was found for the chemically modified filler at 7.5 w.% concentration. Here the absolute increase of F_{max} was found to be from 30.50 MPa to 32 MPa for deformation rate of 50mm/s. In the filler concentration range of 2.5 to 7.5 w.% a plateau region of F_{max} was found, indicating highest mechanical strength of the studied material for both deformation rates. A minor effect was found for chemically + plasma treated filler. However, by plasma treatment the mechanical strength as indicated by F_{max} parameter was continuously decreasing from 31 MPa at 2.5 w.% filler content to 30.18 MPa at 15 w.% filler content. A similar pattern was found for LLDPE polymer composite as shown in Figure 2. Results of the latter experiments are summarized in Tables 2-4.

However, for higher deformation rates the tensile strength was increased, suggesting lowered mobility of the macromolecular chains. This triggers their higher stiffness as reflected by a three fold decrease of elongation at break with increasing degree of filling from the initial value of 24 % to 7,8 % as obtained for 50 mm/min deformation rate (see Fig.3). A similar decreasing trend of elongation at break was found also for deformation rate of 200 mm/min by factor of 3 for both composites under study.

The Elastic modulus (Fig.5 and Fig.6) increased with the increasing filler content, which can be attributed to improvement in stiffness of kaolin/polymer composites, as reported earlier by Das *et al*. [26]. This was observed for both studied composites in a similar fashion. This observed increase of the modulus is a result of the increased brittleness of the samples as reflected in decreasing elongation at break for both studied polymer matrices and in the whole filler concentration range.

Fracture toughness measurements were performed at room temperature of 24°C. It was found that the fracture toughness of both the studied composite systems (virgin kaolinite, plasma treated kaolinite and their silane modifications as fillers) steadily increased with increasing filler content. We must consider a complex nature of the observed behaviour, where for concentrations 10 w.% a maximum value was found to be 22 kJ/m^2 and 18 kJ/m^2 respectively. A graphical representation of the latter dependencies is shown in Figures 7 and 8.

To follow the macroscopic changes of the polymer matrix the SEM measurements were performed. These are shown in Figures 9 to 12. As is very well known, for mechanical behaviour of

5

polymers, it is typical its time dependency, already from small deformations. What are important here are irreversible deformations, which are generated after exceeding the limiting value, in the case of solid polymers known as upper yield stress. However, we are not able to describe the polymer plasticity only by mechanical friction of structural elements, due to the fact that in comparison to the real mechanical friction it is time and temperature dependent. External stresses create permanent changes in the structure of polymer materials. The latter structural changes are either localized or they target wider volume of the body. Local damage leads to the fracture, while permanent changes act at the wider volume and mostly have the character of the plastic deformation. A typical pattern observed for HDPE is shown in Figure 9, where individually localized shearing bands were found. If the material consistency is accompanied by wider plastic deformation, then ductile fracture is observed. In contrast to the latter ductile fracture, the fracture proceeding in the elastic deformation area is the brittle fracture. In all experiments performed in this study, no observations of purely brittle fracture were found. Ability to undergo plastic deformation is very important for practical applications of polymer materials, because it allows absorption and scattering of the mechanical energy into the large polymer volume thus protecting its concentration into the area of hazardous craze. It is responsible for effective mechanical energy dissipation in the material body. As can be seen in Fig 10 and 12, HDPE and LLDPE/kaolin composite modified of (3-aminopropyl) triethoxysilane with 7.5 w.% degree of filling revealed a homogenous distribution of kaolin when incorporated in the synthetic polymer matrix. Stress concentration develops around the particles under the effect of external load and actual stress distribution explores the local micro-mechanical deformation processes in heterogeneous polymer systems similarly as in the previous paper [27]. According to the literature, in particulate filled polymers the dominating deformation mechanism is the separation of the matrix/filler interface, i.e. debonding, which leads to a volume increase during deformation [28]. However, in this study, we have found for all samples an excellent polymer/filler adhesion, resulting in creation of small crazes at the end part of the filler particles immersed in the matrix, oriented perpendicularly to the applied mechanical deformation. This behaviour is typical for ductile fracture mechanism. As visible from Figures 10 and 12 typical crazes were localized at the edges of the mineral filler particles (kaolinite) which were acting as the points of the stress localization during mechanical tensile testing. At the beginning of the deformation process distortion plasticity yield belts oriented in the direction of the maximum shear stress (obliquely to the tensile direction) were observed (see Figures 9 and 11) for both HDPE and LLDPE polymer samples. These then may continue their development by means of the neck propagation. However, at the higher deformations in the case of the filled polymer matrices similarly as in the case of virgin HDPE and LLDPE typical crazes were found (see Figures 10 and 12). Plastically deformed fortified material

6

is a natural barrier against growth of the crack. The magnitude of such a barrier also depends on testing body geometry. In the case of the planar tightness plastic zones can be most fully developed. In contrary at the conditions of the planar deformation, which are prevailing in the central layer of the thick board, suppress plasticity and favours initiation of the brittle fracture. However, there is not a clear sharp boundary between localized (brittle) and volume (ductile) dislocation. Even at the brittle (or quasi-brittle) fracture it is possible to find at the fracture area layers of plastically transformed (oriented) polymer. However a plastic deformation never covers the whole volume of the testing body evenly.

In Table 5 are summarized results of the thermal analysis of the studied PE composite systems. There were determined parameters such as melting point temperature (T_m), enthalpy of fusion at the melting point (ΔH_m), degree of crystallinity, position of the first exothermic peak T_{exo} and degree of crystallinity (Xc) calculated according to Jung et al. [29-31]. As given in Table 5, with increasing degree of filling of PE polymer macromolecular matrix a decrease of the fusion enthalpy was found to be accompanied with a decrease of the melting point temperature. This fact indicates successful disruption of the PE macromolecular oriented higher degree structure. When crystallized from dilute solution, PE polymers display the characteristic platelet or lamella structure. It has been well established, that the chain axes are preferentially normal to the wide faces of the lamella. Hence, a given polymer molecule must traverse a crystallite many times. Based on earlier electron microscopy observations, it has been presumed that this interface is comprised of regularly folded chains. However approximately 15-20% of the chain units must be in non-ordered conformations. This triggers the conclusion that the presence of such a large number of non-crystalline chain units leads to the presence of a disordered amorphous overlayer [30]. The above conclusions correspond well to our findings as with an increasing degree of filling the crystallinity decreased as well (see Table 5).

5 Conclusions

The effect of low temperature air plasma treatment and silane coupling agent modification of the surface properties of kaolin based nano filler used for preparation of polyethylene composites (both HDPE as well as LLDPE) was studied. The effect on the final composite physico-chemical, mechanical and thermal properties was studied over a wide range of degrees of filling. It was found that the silane coupling agent surface modification had the strongest effect resulting in improved mechanical properties. Mainly the improvement of the fracture toughness of prepared HDPE and LLDPE kaolinite composites was confirmed. Simultaneously there was also found a tensile strength and elastic modulus increase with increasing degree of filling. Dispersion quality and the morphology of the fracture interface were confirmed by SEM experiments. Here, typical shearing bands due to the

7

progressing plastic deformation of the PE macromolecules were found which in the case of the presence of the filler kaolin particles generate cracks creation due to the brittle mode of the fracture process.

6 Aknowledgements

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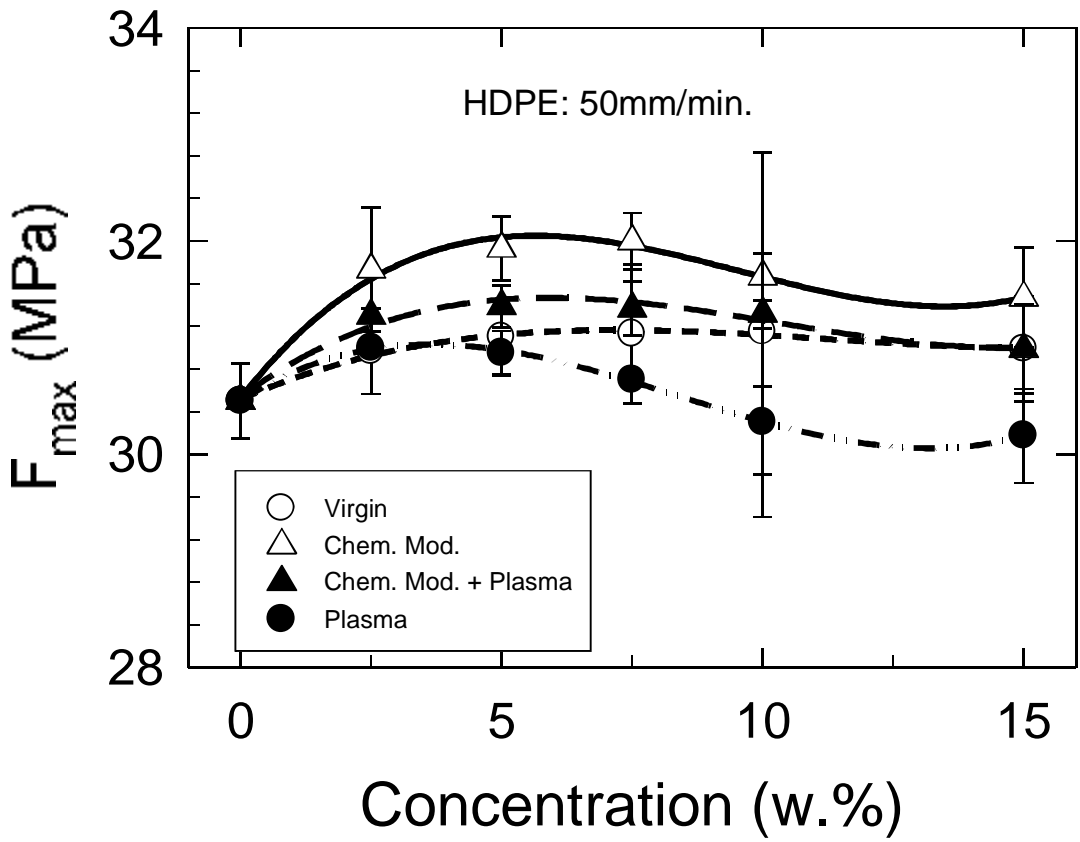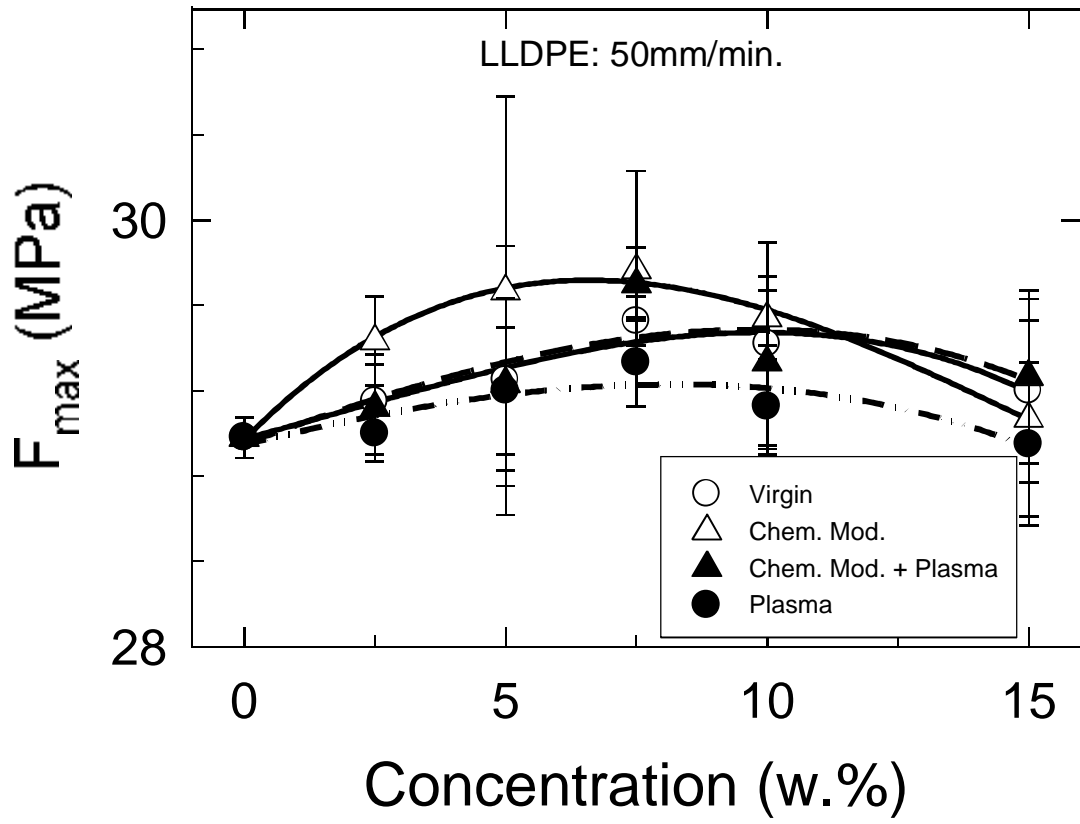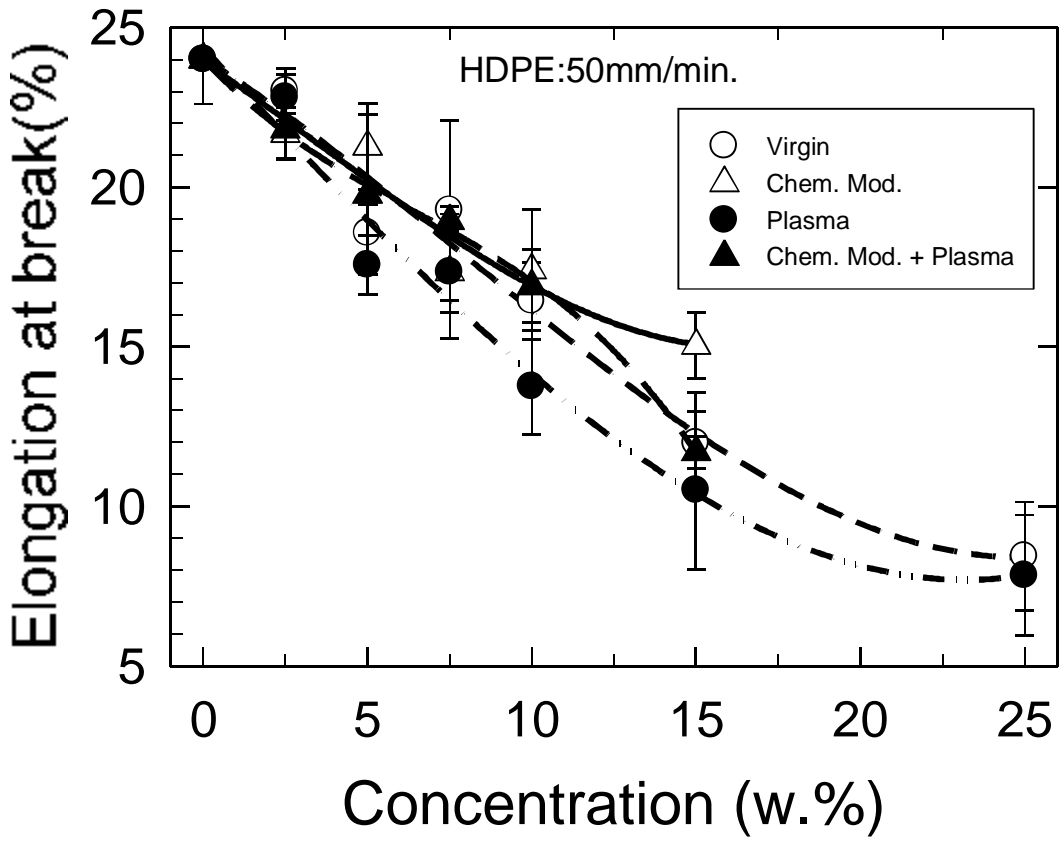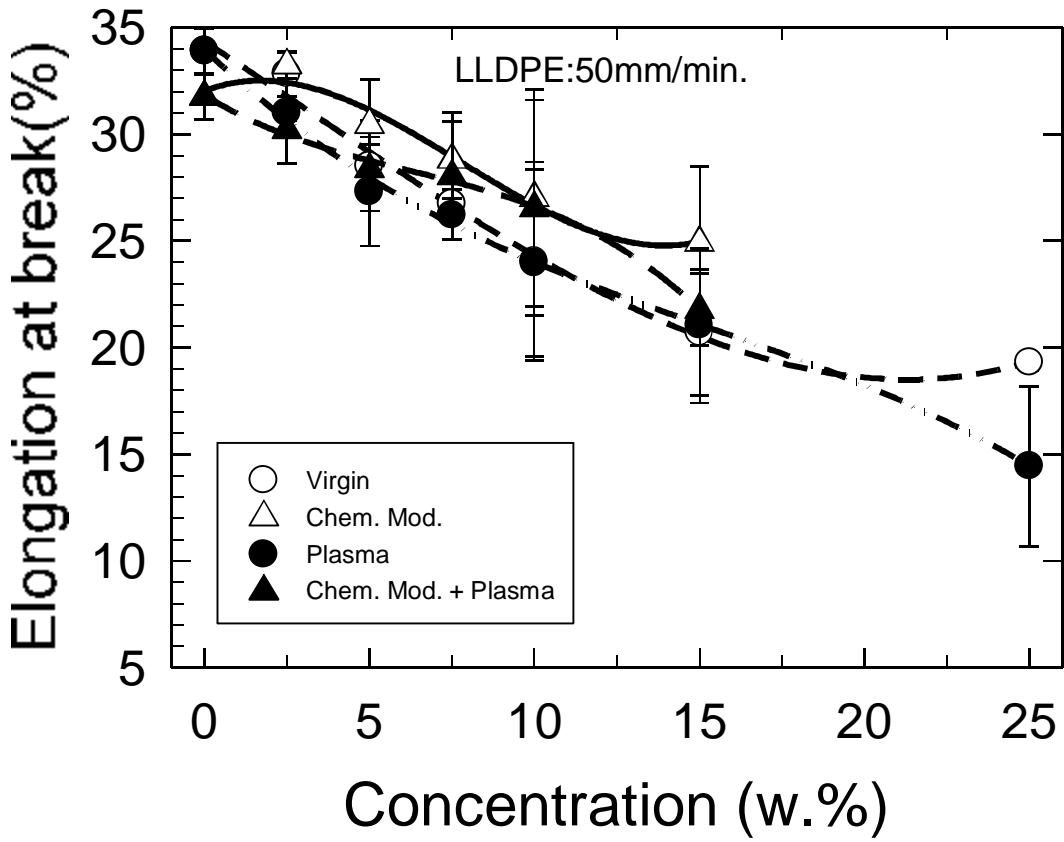53
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<u>Figure caption:</u>

Fig.1: Kaolin filler concentration dependence of the ultimate tensile strength (Fmax) for HDPE at a
deformation rate of 50 mm/min.

Fig.2: Kaolin filler concentration dependence of the ultimate tensile strength (F_{max}) for LLDPE at a
deformation rate of 50 mm/min.

Fig.3: Kaolin filler concentration dependence of the elongation at break for HDPE at a deformation
rate of 50 mm/min.

Fig.4: Kaolin filler concentration dependence of the elongation at break for LLDPE at a deformation
rate of 50 mm/min.

Fig.5: Kaolin filler concentration dependence of the elastic modulus (E) for LLDPE in deformation
rate of 50 mm/min.

Fig.6: Kaolin filler concentration dependence of the elastic modulus (E) for HDDPE in deformation
rate of 50 mm/min.

Fig.7: Fracture toughness of HDPE composite as a function of kaolinite filler concentration
dependence.

Fig.8: Fracture toughness of LLDPE composite as a function of kaolinite filler concentration
dependence.

Fig.9: SEM images of HDPE fracture surface.

Fig.10: SEM image of HDPE/silane coupling agent modified kaolinite fracture surface.

Fig.11: SEM image of LLDPE fracture surface.

Fig.12: SEM image of LLDPE/silane coupling agent modified kaolinite fracture surface.

HDPE: 50mm/min.

F_{max} (MPa)

Concentration (w.%)

	Virgin
	Chem. Mod.
	Chem. Mod. + Plasma
	Plasma

Fig. 1.

LLDPE: 50mm/min.

Legend:
○ Virgin
△ Chem. Mod.
▲ Chem. Mod. + Plasma
● Plasma

Axis labels: F_{max} (MPa) vs Concentration (w.%)

Fig.2.

Fig.3.

Fig.4.

Fig.5.

Fig.6.

Fig.7.

Fig.8.

HDPE_c-03 1.0kV 7.6mm x6.00k SE   5.00um

Fig.9.

HDPE_m-11 1.0kV 7.0mm x4.50k SE   10.0um

Fig.10.

LLDPE_c-08 1.0kV 7.5mm x1.20k SE   40.0um

Fig.11.

Fig.12.

Table caption:

Table 1: Processing parameters of injection molding machine.

Table 2: Mechanical properties of HDPE samples with different untreated kaolinite filler contents.

Table 3: Mechanical properties of HDPE samples with different plasma treated kaolinite filler contents.

Table 4: Mechanical properties of silane coupled HDPE samples modified with different untreated kaolinite filler contents.

Table 5: Results of the TG DTG experiments of studied HDPE/kaolin and LLDPE/kaolin composites.

Table 1: Processing parameters of injection molding machine

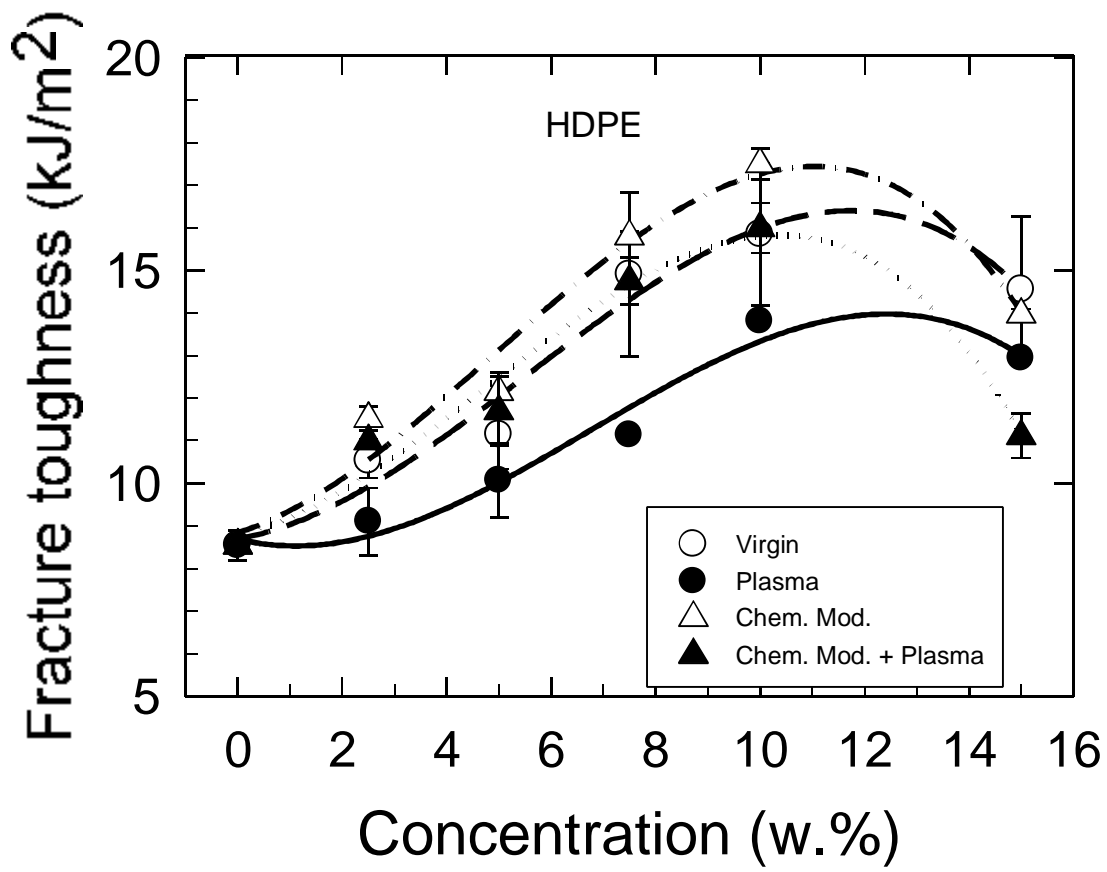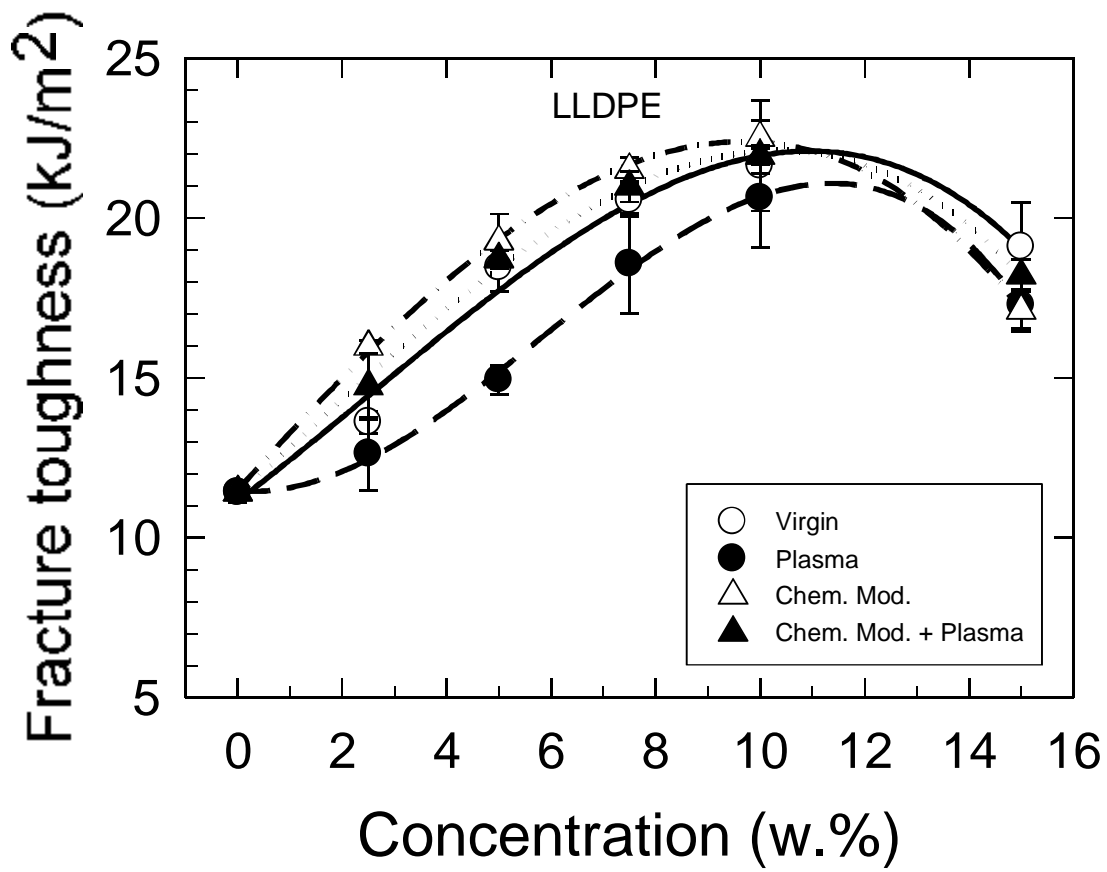|	HDPE	LLDPE
Temperature (°C)	160-180	200-230
Injection speed (mm/s)	50.0	40.0
Pressure (bar)	1000	1200
Cooling time (s)	15	15

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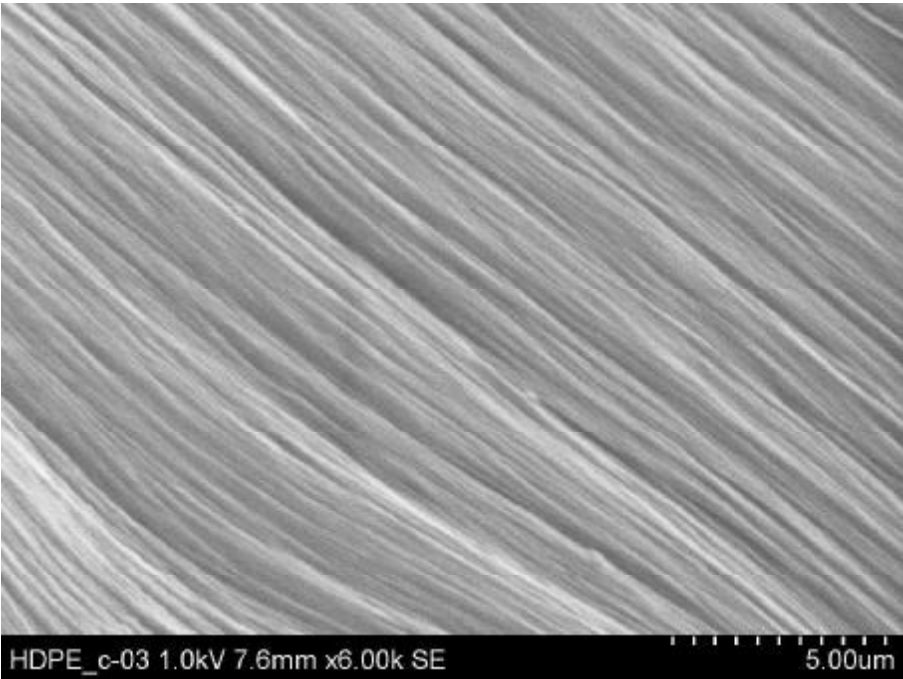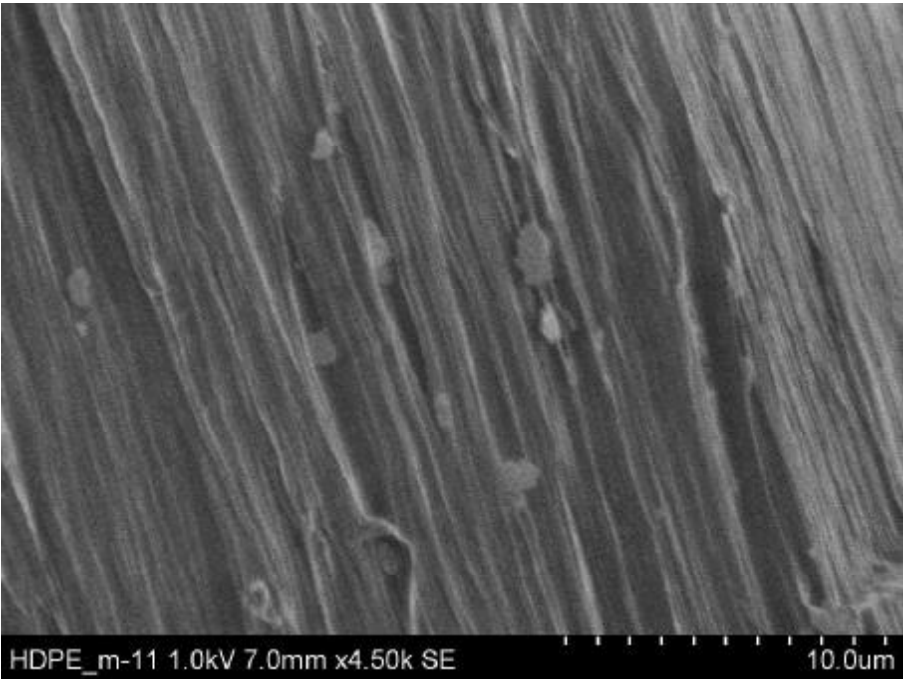46
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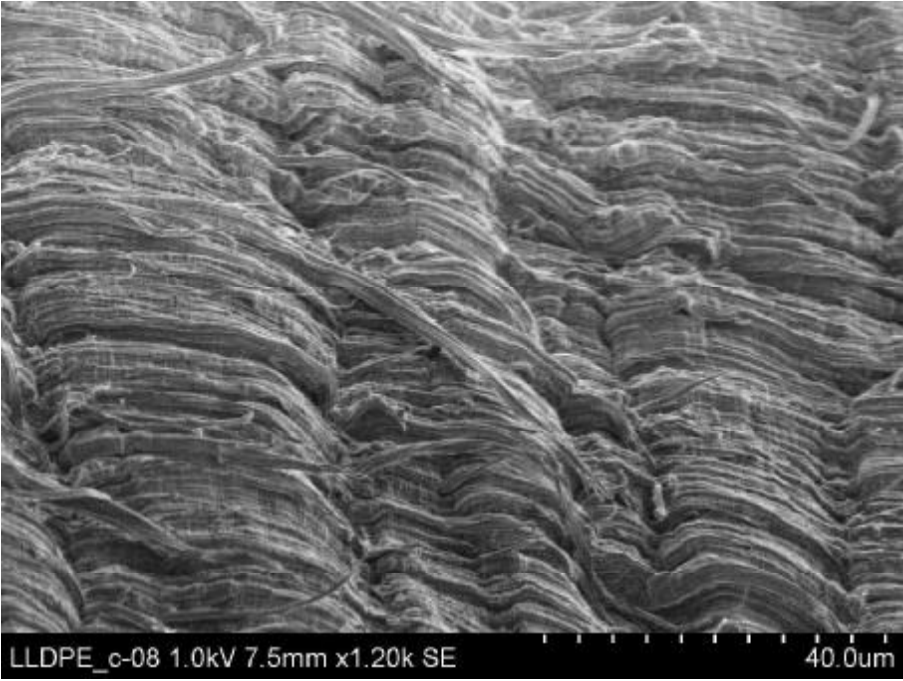53
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Table 2: Mechanical properties of HDPE samples with different untreated kaolinite filler contents.

| Filler concentration (wt. %) | Deformation rate (mm/min) | | | | | |
| | 50 | | | 200 | | |
	F_{max}(MPa)	ε (%)	E (MPa)	F_{max}(MPa)	ε (%)	E (MPa)
0	30.50±0.17	24.00±0.34	1523.00±2.54	33.10±0.10	17.13±0.27	1635.00±2.00
2.5	30.97±0.26	23.00±0.44	1799.33±1.08	33.73±0.16	16.33±0.29	1789.33±2.14
5	31.10±0.17	18.55±0.27	1902.50±2.89	33.78±0.21	13.28±0.30	1862.50±1.79
7.5	31.13±0.33	19.27±0.69	1957.67±2.77	33.47±0.33	12.30±0.29	1863.33±2.74
10	31.15±0.21	16.43±0.32	1987.50±1.58	33.08±0.27	10.50±0.44	1897.50±1.63
15	30.99±0.20	11.98±0.37	2027.50±2.39	33.00±0.34	8.00±0.33	1922.50±2.30
25	30.67±0.31	8.43±0.53	2043.33±3.29	31.77±0.38	6.73±0.43	1900.66±2.05

F_{max} – ultimate tensile strength, ε – elongation at break, E – elastic modulus

Table 3: Mechanical properties of HDPE samples with different plasma treated kaolinite filler contents.

Filler concentration (wt. %)	Deformation rate (mm/min)					
	50			200		
	F_{max} (MPa)	ε (%)	E (MPa)	F_{max} (MPa)	ε (%)	E (MPa)
0	30.50±0.17	24.00±0.34	1523.00±2.54	33.10±0.10	17.13±0.27	1635.00±2.00
2.5	31.00±0.08	22.80±0.35	1630.67±0.98	33.50±0.25	15.33±0.57	1673.33±2.42
5	30.95±0.19	17.55±0.39	1696.67±2.33	33.47±0.49	12.07±0.48	1696.67±2.26
7.5	30.70±0.10	17.33±0.46	1770.00±2.40	33.03±0.28	11.33±0.28	1730.00±2.76
10	30.30±0.27	13.75±0.50	1785.00±2.03	32.35±0.20	9.93±0.34	1775.00±2.04
15	30.18±0.19	10.50±0.45	1907.50±2.56	31.83±0.31	7.63±0.41	1695.33±1.29
25	29.67±0.41	7.83±0.78	1997.67±2.63	31.67±0.34	7.80±0.42	1680.00±2.42

F_{max}= ultimate tensile strength; ε= elongation at break; E= elastic modulus

Table 4: Mechanical properties of HDPE/kaolinite samples modified with silane coupling agent (3-aminopropyl)triethoxysilane.

Filler concentration (wt. %)	Deformation rate (mm/min)					
	50			200		
	F_{max} (MPa)	ε (%)	E (MPa)	F_{max} (MPa)	ε (%)	E (MPa)
0	30.50±0.35	24.00±0.14	1523.00±2.54	33.10±0.10	17.13±0.27	1635.00±2.00
2.5	31.73±0.58	21.67±0.25	1843.67±2.71	33.93±0.26	16.43±0.53	1767.33±1.81
5	31.93±0.29	21.27±0.19	1923.67±2.33	34.03±0.19	14.40±0.30	1845.33±1.91
7.5	32.00±0.26	17.33±0.06	1960.00±1.70	33.83±0.31	14.39±0.37	1886.67±1.60
10	31.67±0.22	17.40±0.10	1990.00±2.10	33.33±0.22	13.30±0.51	1943.33±2.26
15	31.47±0.09	15.03±0.15	2006.50±1.93	33.32±0.23	13.07±0.61	1965.00±1.29

F_{max} – ultimate tensile strength, ε – elongation at break, E – elastic modulus

Table 5: Results of the TG DTG experiments of studied HDPE/kaolin and LLDPE/kaolin composites.

Filler concentration (wt. %)	HDPE/virgin kaolin				
	Weight loss (%)	T_m (°C)	ΔH_m (J/g)	T_{exo} (°C)	X_c (-)
0	100.0	131.5	-196.2	-	0.670
5	91.2	132.2	-180.0	258.3	0.614
10	97.7	132.0	-184.9	255.0	0.631
15	88.0	131.5	-171.2	241.3	0.584
25	86.7	132.0	-170.8	246.0	0.583
HDPE/kaolin 10 min. air plasma treated					
5	95.7	132.0	-188.6	265.0	0.635
10	90.7	132.3	-177.5	247.3	0.644
15	89.0	131.6	-180.1	238.8	0.606
25	95.3	130.7	-186.1	264.7	0.615
LLDPE/virgin kaolin					
0	100.0	130.5	-189.5	-	0.647
5	93.2	130.2	-194.4	241.0	0.663
10	84.7	130.2	-160.9	231.0	0.549
15	89.3	130.4	-161.8	242.1	0.552
25	84.6	130.0	-172.4	245.8	0.588
LLDPE/kaolin 10 min. air plasma treated					
5	93.7	134.4	-181.2	248.7	0.555
10	84.8	133.4	-167.0	237.1	0.618
15	84.6	130.5	-159.1	251.2	0.570
25	89.6	130.2	-162.5	237.3	0.543