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Novel engineering approaches on composite materials (Part I)

Effect of low temperature air plasma treatment on physico-chemical properties of kaolinite/polyethylene composites

Lubomir Lapcik[1,2], **Barbora Lapcikova**[1,2], **Ivo Krasny**[2] **Ivana Kupska**[2]

[1]Center of Polymer Systems, Tomas Bata University in Zlin, Faculty of Technology,
Nam. T.G. Masaryka 5555, 760 01 Zlin, Czech Republic
lapcik@ft.utb.cz
[2]Tomas Bata University in Zlin, Faculty of Technology, Institute of Foodstuff Engineering,
Nad Stranemi 4511,760 05 Zlin, Czech Republic

ABSTRACT

It was found in this study that air plasma treatment of particular kaolinite has led to the change of its wettability. This was reflected in the decreased values of water contact angles of wetting. There were determined yield locus and flow function dependencies at different stress levels for virgin and different time plasma treated samples (flow index - *ffc*, effective angle of internal friction - phi_e, unconfined yield strength - sigma_c). It was found that by plasma treatment the character of the flow was shifting from region of very cohesive (*ffc* = 2.39) to the cohesive (*ffc* = 3.19). For untreated samples effective angle of internal friction was decreased with increasing applied consolidation stress, while for plasma treated kaolinite it was increased. As a result of the latter powder rheological changes was a notable improvement of the fracture toughness of prepared HDPE composites as found in the whole concentration range of degree of filling under study (from 5 to 25 w.% filler concentration) and tensile strength increase found for 5 w.% virgin kaolinite filled polyethylene composites. This improvement to the fracture toughness became more marked as the filler loading increased, indicating an improved degree of filler/matrix interaction.

Keywords: *composites; mechanical properties, poly(ethylene) (PE);kaolinite*

1 Introduction

Characterization and modification of polymers are perhaps the most important aspects of polymer research, production and applications. Polymeric materials, especially thermoplastics have become an essential part of our everyday lives. They combine good mechanical and electrical properties with low density and high formability. Thermoplastics, as implied by their name, are materials that flow upon heating, and harden when cooled. They can be formed using a wide variety of techniques, such as injection moulding, thermoforming, blow moulding, and rotational moulding. As well as being easily processed when molten, they also have the potential to be recycled by re-melting them to form new articles, or burnt and used to generate electrical energy.[1,2] Polyethylene (PE) and polypropylene (PP) are the world's number one and two highest volume thermoplastics, respectively, and they are also the least expensive per unit volume.[2] PE is, by a wide margin, the largest volume synthetic polymer made by mankind. It has excellent flexibility, considerable chemical resistance and high transparency. [3,4] Based on its density and branching, PE is roughly classified into four different categories, high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), and very low density polyethylene (VLDPE).[6]

High density polyethylene (HDPE) is produced by polymerization of ethylene using Ziegler-Natta or supported chromium ("Phillips") catalysts. HDPE cannot be produced by free radical polymerization. Density is typically of 0.94-0.97 g/cm^3. Small amounts (<1%) of α-olefin co-monomers are used in many of the commodity grades to introduce low concentrations of short chain branching, primarily to enhance processability but also to improve toughness and environmental stress crack resistance. HDPE has high modulus, yield and tensile properties relative to LLDPE. HDPE is widely used in extruded pipe for potable water and gas distribution. Another important application is in blow moulded packaging for household and industrial chemicals, such as bottles for bleach, shampoo, detergent, etc.[2,3,6]

Linear Low Density Polyethylene (LLDPE) is produced by copolymerization of ethylene with α-olefins using Ziegler-Natta, supported chromium or single site catalysts. LLDPE cannot be produced by free radical polymerization. Density is typically of 0.915-0.930 g/cm^3. Butene-1, hexene-1 and octene-1 are the most common co-monomers, resulting in LLDPE with short chain branches of ethyl, -butyl and n-hexyl groups, respectively. The quantity of co-monomer incorporated varies depending upon the target resin. Density decreases as greater amounts of co-monomer are incorporated into the copolymer. LLDPE has improved mechanical properties relative to low density polyethylene and is used in blown and cast film applications, such as food and retail packaging[2,3,6].

In the last years, the clay minerals and their surface modification are widely used in catalysis, as adsorbents, in sensors and as filler in polymer-clay composite systems.[5] Matrix modification, type of reinforcement and its adhesion, addition of coupling agents influence physical, chemical and thermal properties of further system[9,10].

The main aim of this work is an effect of low temperature air plasma treatment on physico-chemical properties of polyethylene/kaolinite composite system with content up to 25wt.% of kaolinite powder's filler.

2 Materials

Industrial polyethylenes are commonly classified and named using acronyms. In this study were studied two commercial polyethylenes: HDPE TIPELIN 6300B (Tiszai Vegyi Kombinat, Hungary) and LLDPE LITEN (Unipetrol PND 33-300, Czech Republic).

Plasma treated and virgin kaolinite (Imerys Minerals Ltd, Cornwall, UK) with a median particle diameter of 3 μm and 0.27 wt. % moisture content was used in this study as a powder's filler. Particle characterization of this clay mineral was in detailed studied (Lapcik et al., 2012; Greenwood R.W. et al.,).[7,8]

3 Methods

3.1 Preparation of Samples

Air plasma treatment of filled powder was performed in Diener Femto (Diener Electronic, Germany) capacitively coupled plasma reactor operating at 13.56 MHz frequency for 10 min. Kaolinite powder was placed into the rotating rectangular parallel piped glass reactor chamber (borosilicate glass cylinder of 320 mm length and 150 mm diameter), which was placed inside the plasma reactor. The processing reactor conditions were as follows: generator power 100 W, air flow rate 5 cm^3/min, processing pressure 35 Pa.[7]

Composites were filled with pure and plasma treated kaolinite powder with content 0, 2.5, 5, 7.5, 10, 15 and 25 wt %. Filled, homogenized polyethylenes were then injection-moulded in a Arburg Allrounder 170 U 150-30 machine (Germany) to a tested samples according to standards CSN EN ISO294-1 and CSN ISO 293. The processing parameters of injection-moulding are shown in Table1.

Table 1: Processing parameters of injection moulding 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

3.2 Tensile Strength Testing

Tensile strength measurements were performed with moulded dog-bone standards using universal testing machine ZWICK 1456. The measurements have been done on series of dog-bones with deformation speed of 50 and 200 mm/min. The average values have been considered. Tensile strength (σ), elongation at break (ε) and elastic modulus (E) of the series composites with increasing filler content have been observed. The results are summarized in Tables 2-3.

3.3 Notched impact toughness

Notched impact toughness measurements were performed on CEAST Resil Impactor Junior (Germany).

4 Results and Discussion

As it was found and in detail described in our paper[7], air plasma treatment of particular kaolinite has led to the changes of its wettability. This was reflected in the decreased values of water contact angles of wetting. There were determined yield locus and flow function dependencies at different stress levels for virgin and different time plasma treated samples (flow index - *ffc*, effective angle of internal friction - phi_e, unconfined yield strength - $sigma_c$). It was found[7] that by plasma treatment the character of the flow was shifting from region of very cohesive (*ffc* = 2.39) to the cohesive (*ffc* = 3.19). For untreated samples effective angle of internal friction was decreased with increasing applied consolidation stress, while for plasma treated kaolinite it was increased. The latter observed modified powder rheological properties were affecting the processing of composite polymer/filler during injection moulding process.

In Tables 2 and 3 are shown results of the tensile strength measurements of virgin and plasma treated kaolinite filler modified HDPE polymer composites. Observed results indicate minor increase of the tensile strength for 5 w.% degree of filling for both deformation rates applied (50 and 200 mm/min). However, for higher deformation rates tensile strength was increased, suggesting lowered mobility of macromolecular chains. This triggers their higher stiffness as reflected by four fold decrease of elongation at break with increasing degree of filling from initial 23.5 % to 6 % as obtained for 200 mm/min deformation rate. Similar decrease of elongation at break was found for smaller deformation rate 50 mm/min by factor of 3.

Fracture toughness measurements were performed at room temperature of 24°C. It was found that the fracture toughness of both studied composite systems (virgin kaolinite, plasma treated kaolinite as fillers) was steadily increasing with increasing filler content. However, this simplified linear approach does not reflects very well the complex nature of the observed behaviour, where for concentrations 10 w.% a maximum value was found of 18 kJ/m^2. Graphical representation of the latter dependencies is shown in Figure 1.

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

Filler concentration (wt. %) (wt	Deformation rate (mm/min)					
	50			200		
	σ(MPa)	ε (%)	E (MPa)	σ(MPa)	ε (%)	E (MPa)
0	31.13±0.17	22.00±0.34	1625.00±2.54	33.73±0.10	14.53±0.27	1735.00±2.00
2.5	30.97±0.26	23.57±0.44	989.33±1.08	33.47±0.16	16.33±0.29	989.33±2.14
5	31.43±0.17	17.55±0.27	1902.50±3.89	34.10±0.21	10.28±0.30	1862.50±1.79
7.5	30.90±0.33	19.27±0.69	1076.67±2.77	32.97±0.33	11.33±0.29	1183.33±2.74
10	31.65±0.21	13.75±0.32	1987.50±1.58	33.08±0.27	10.50±0.44	1897.50±1.63
15	30.90±0.20	10.50±0.37	2027.50±2.39	33.00±0.34	8.00±0.33	1922.50±3.30
25	30.67±0.31	8.43±0.53	2243.33±3.29	31.77±0.38	6.73±0.43	2246.66±5.05

σ = 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. %) (wt	Deformation rate (mm/min)					
	50			200		
	σ(MPa)	ε (%)	E (MPa)	σ(MPa)	ε (%)	E (MPa)
0	31.13±0.17	22.00±0.34	1625.00±2.54	33.73±0.10	14.53±0.27	1735.00±2.00
2.5	30.97±0.00	23.00±0.35	1016.67±0.98	33.47±0.25	15.33±0.57	1013.33±2.42
5	31.43±0.19	18.57±0.39	1696.67±6.33	34.10±0.49	12.07±0.48	1696.67±2.26
7.5	30.90±0.10	17.33±0.46	1070.00±2.40	32.97±0.28	12.30±0.28	1090.00±2.76
10	31.65±0.27	16.43±0.50	1785.00±2.03	33.08±0.20	9.93±0.34	1775.00±2.04
15	30.90±0.19	11.98±0.45	1907.50±3.56	33.00±0.31	7.63±0.41	2073.33±3.29
25	30.67±0.41	7.83±0.78	2086.67±5.63	31.77±0.34	7.80±0.42	1960.00±3.42

σ = tensile strength; ε= elongation at break; E= elastic modulus.

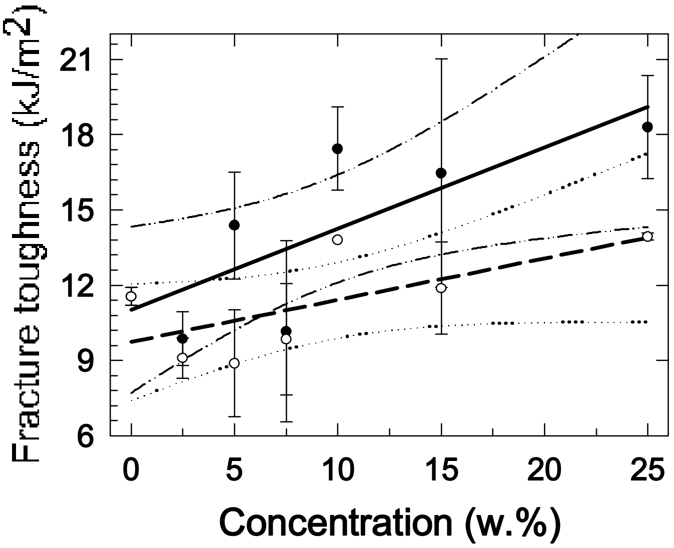

Figure 1: Fracture toughness of HDPE composite kaolinite filler concentration dependence: full circles – virgin kaolinite, empty circles – 10 minutes air plasma treated kaolinite. Measurements were performed at 24°C. Dotted lines 95 % confidential interval.

5 Conclusions

There was found improvement of the fracture toughness of prepared HDPE-kaolinite composites in this study in the whole concentration range of degree of filling ranging from 5 to 25 w.% filler concentration. Simultaneously there was found also tensile strength increase for 5 w.% virgin kaolinite filled polyethylene composites. This improvement to the fracture toughness became more marked as the filler loading increased, indicating an improved degree of filler/matrix interaction.

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