

High-Density Polyethylene Filled with Modified Chalk

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Synopsis

High-density polyethylene was filled with chalk in various concentrations ranging from 10% to 60% by weight. Ethylene oxide oligomer $M_w = 300$ was used as a liquid modifier for chalk in the amount $0 \div 20$ wt % of the filler. The mechanical properties of these composites showed that high density polyethylene filled with chalk have quite high ultimate elongation and impact strength while their elastic modulus and tensile strength are very near to those values for pure high density polyethylene. On the base of mechanical properties and microscopical observations, the crack and microcrack damping is attributed to the presence of ethylene oxide oligomer.

INTRODUCTION

Fillers are generally added to polymers to improve their physicomechanical properties, processability, and/or to lower the cost. The commonly used fillers, for polyolefines, are talc,¹ calcium carbonate,² asbestos,³ kaolin,⁴ metal powders,⁵ metal oxides,⁶ aluminium hydroxide,⁷ mica,⁸ glass fibers,⁹ silica,¹⁰ carbon black,¹¹ cellulose,¹² lignin,¹³ and peanut shells.¹⁴ Mineral fillers tend to increase the modulus of elasticity and hardness of the composites, which makes the final product weak and crunchy. Thus, the surface of the filler particles should be treated to improve the quality of the filler-polymer interfaces. Among these are the covering of the filler particles by modifiers, for example, covering the filler particles by a layer of organic titanates,¹⁵ stearic acid and its sodium, calcium and barium salts, complex compounds of magnesium or aluminium silicates,¹⁶ by silane coupling agents,^{17,18} or by polymeric layer,¹⁹⁻²² where the second polymer could be introduced as a monomer. The monomers commonly used are pyridine, divinyl benzene, styrene, acrylic acid, methacrylic acid, and their esters. The monomers could be polymerized according to the free radical mechanism catalyzed by the conventional initiators or according to cationic mechanism initiated by activated mineral surface. The polymer layer could also be introduced in a separate technological process or, as in the case of polyolefines, during their mixing with fillers.²³

More recently, fillers are modified by a liquid.²⁴ The liquid used has the advantage that it wets well both the polymer and the filler particles; the liquid layer around the chalk particles inhibits the fracture phenomena,²⁵ i.e., inhibits the crack initiation and propagation. These lead to high impact strength and elongation at break of the composites. The effect of liquid interface on the mechanical properties of the composites was already shown for polypropylene

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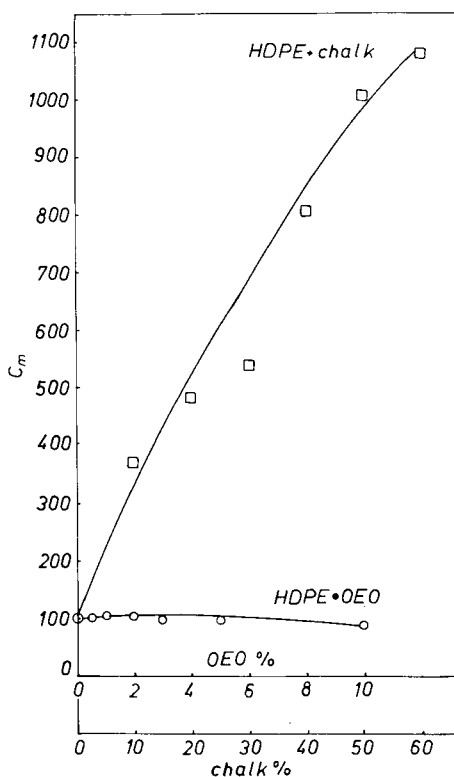


Fig. 1. The dependences of modulus of elasticity of high-density polyethylene filled with chalk on the concentration of chalk and of high-density polyethylene filled with oligomer of ethylene oxide on the concentration of OEO. Both curves scaled to the value of modulus of pure HDPE.

filled with chalk, talc, and kaolin²⁴ and for low-density polyethylene filled with chalk.²⁵ Ethylene oxide oligomer was found to be the most suitable liquid. The composite samples exhibit typical thermoplastic materials behavior: necking and plastic deformation.

In the present work, chalk was modified by an oligomer of ethylene oxide and the modified chalk was mixed with high-density polyethylene; the prepared composites were evaluated by measuring the mechanical properties.

EXPERIMENTAL

Materials

High-density polyethylene (HDPE) (a BASF product Luplen 6011L, melt index 4.5–6 according to ASTM-D 1238-67T, density 0.961 g/cm³, 0.2 CH₃-side groups/1000 C in the main chain) was filled with various amounts of precipitated chalk (Polish product, 96.1% of the particles below 15 μm). An oligomer of

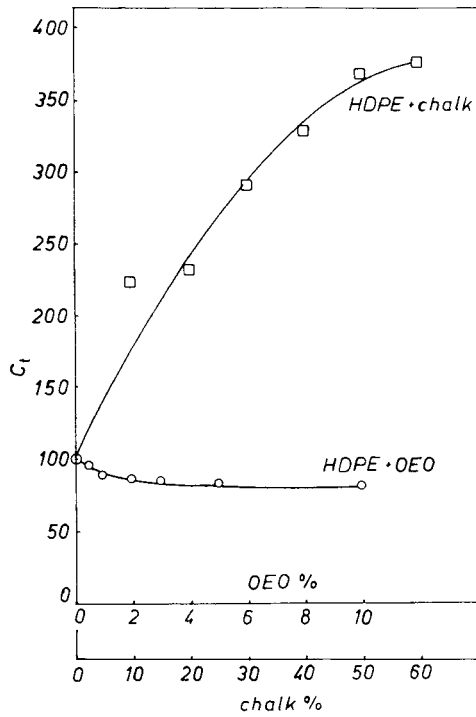


Fig. 2. The dependences of tensile strength of high-density polyethylene filled with chalk on the concentration of chalk and high-density polyethylene filled with oligomer of ethylene oxide on the concentration of OEO. Both curves scaled to the value of tensile strength of pure HDPE.

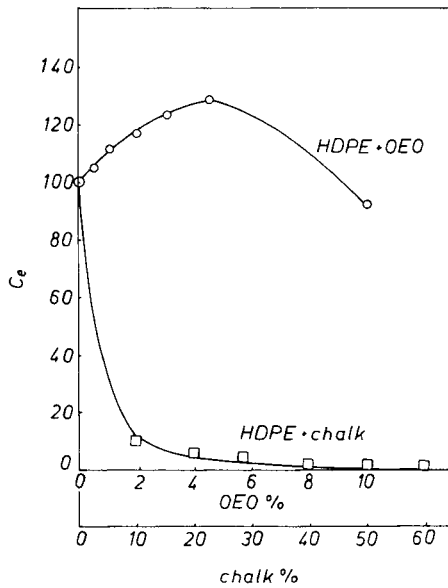


Fig. 3. The dependences of ultimate elongation of high-density polyethylene filled with chalk on the concentration of chalk and high-density polyethylene filled with oligomer of ethylene oxide on the concentration of OEO. Both curves scaled to the value of ultimate elongation of pure HDPE.

ethylene oxide (OEO) (Polish product, mol wt 300, bp 260°C, freely soluble in water) was used for modification of chalk.

Sample Preparation

Chalk was suspended in water and the required amount of OEO (0.5–20%, by weight) was added. The thick pulp was dried in an oven at 85°C till constant weight.

The unmodified and modified chalk was thoroughly mixed with HDPE granules and then extruded at 150°C.

The following samples were prepared:

(1) HDPE modified by 0–10% of OEO, by weight. HDPE containing higher OEO concentrations could not be prepared because of exudation of the latter.

(2) Composites of HDPE with unmodified and modified chalks were prepared in various concentrations ranging from 10% to 60%, by weight.

The samples for the mechanical measurements were prepared by mold pressing

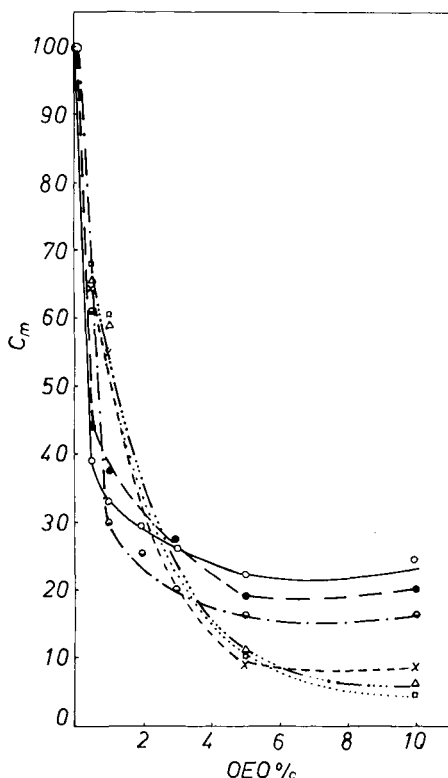


Fig. 4. The dependences of modulus of elasticity of high-density polyethylene filled with various amounts of chalk modified with oligomer of ethylene oxide on the concentration of oligomer of ethylene oxide. Each curve scaled to the value of the modulus of elasticity of the HDPE sample containing the respective percentage of unmodified chalk: (O, —) 10; (●, --) 20; (⊙, ---) 30; (×, -·-·-) 40; (Δ, —·-·-) 50; (□, ····) 60.

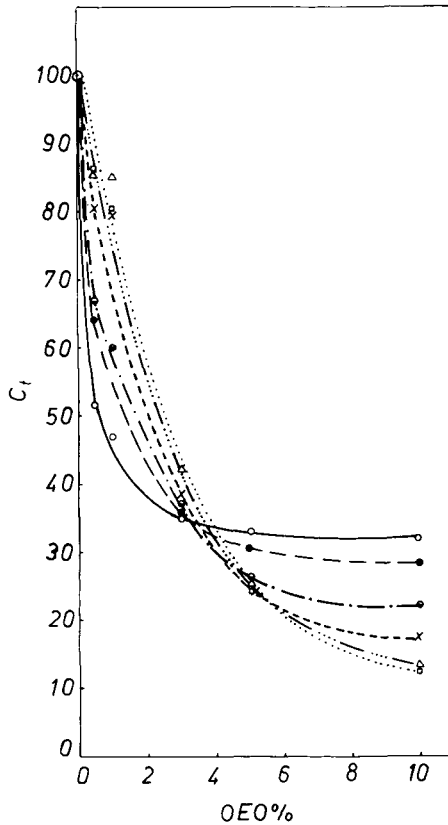


Fig. 5. The dependences of tensile strength of high-density polyethylene filled with various amounts of chalk modified with oligomer of ethylene oxide on the concentration of oligomer of ethylene oxide. Each curve scaled to the value of the tensile strength of the HDPE sample containing the respective percentage of unmodified chalk: (O, —) 10; (●, - -) 20; (⊖, - - -) 30; (×, - - -) 40; (Δ, — ··· —) 50; (□, ···) 60.

at 130°C under pressure of 100 kg/cm² in the form of sheets 0.4 and 4.0 mm in thickness, then punched to dumbbell shape or machined in the form of bars.

Measurements

An Instron-Tensile Testing Machine 1113 was used for measuring the tension tests. The samples were tested according to ASTM-D638 at room temperature with a crosshead speed of 10 mm/min. The mean value of five measurements was taken.

A Werkstoffprüfmachinen-Impact Tester 400/13 was used for measuring Charpy impact strength. The tests were done according to ASTM-D 256 using notched samples. The samples were tested at room temperature, and the mean value of 10 measurements for each group of samples was taken. The face of fractured bars were observed in polarizing optical and scanning electron microscopes.

TABLE I
 Modulus of Elasticity E (kg/mm²), Tensile Strength σ (kg/mm²) and Elongation at Break, ϵ (%) of HDPE, HDPE—Chalk, and HDPE-Modified Chalk Composites

OEO (%)	Chalk (%)														
	0%			10%			20%			30%			50%		
	E	σ	ϵ	E	σ	ϵ	E	σ	ϵ	E	σ	ϵ	E	σ	ϵ
0	51.2	2.14	930	199.0	4.51	96	250	5.00	55	278.0	5.19	35	519.9	7.90	6
0.5	52.4	2.08	980	77.4	2.37	286	110.0	3.21	110	170.1	3.48	69	340.6	6.75	8
1.0	52.8	1.88	1040	60.5	2.12	331	94.8	2.48	131	82.0	3.12	81	307.0	6.74	9
2.0	55.8	1.86	1090	59.3	1.78	347	—	—	—	70.1	2.52	97	261.0	4.66	13
3.0	51.9	1.83	1150	51.9	1.61	369	69.9	1.77	156	55.7	1.90	104	242.8	3.30	17
5.0	50.1	1.82	1200	44.0	1.51	403	47.3	1.53	252	46.4	1.37	161	57.2	1.91	23
10.0	47.3	1.74	850	48.8	1.46	1005	50.0	1.44	649	45.6	1.19	417	32.8	1.09	78
20.0	—	—	—	56.1	1.56	980	45.8	1.43	561	39.5	1.14	358	30.2	0.92	255

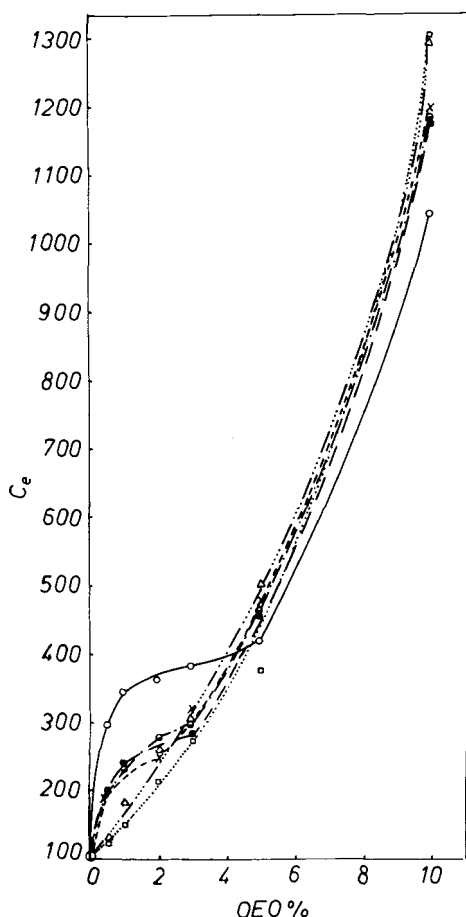


Fig. 6. The dependences of ultimate elongation of high-density polyethylene filled with various amounts of chalk modified with oligomer of ethylene oxide on the concentration of oligomer of ethylene oxide. Each curve scaled to the value of ultimate elongation of the HDPE sample containing the respective percentage of unmodified chalk: (O, —) 10; (●, - -) 20; (○, - · -) 30; (×, · · ·) 40; (Δ, — · · · —) 50; (□, · · ·) 60.

RESULTS

In Figures 1, 2, and 3, the dependence of modulus of elasticity tensile strength and ultimate strain on the concentration of chalk in composites are presented. The plotted values are scaled to that of pure HDPE for easy comparison. The figures show that the addition of 10%, 20%, and 50% of unmodified chalk to HDPE increases its modulus of elasticity by 3.7, 4.8, and 11.9 times, respectively, and its tensile strength by 2.2, 2.3, and 3.7 times respectively, but decreases the elongation at break to 0.1, 0.06, and 0.007 times of the initial values (corresponding to HDPE), respectively. This phenomenon is characteristic for the system of soft polymer matrix filled with tough filler particles and adhering well to the polymer.

The same figures show the relations between the OEO content in HDPE and modulus of elasticity, tensile strength, and elongation at break. One can notice that OEO alone has a small effect on the modulus of elasticity of HDPE but

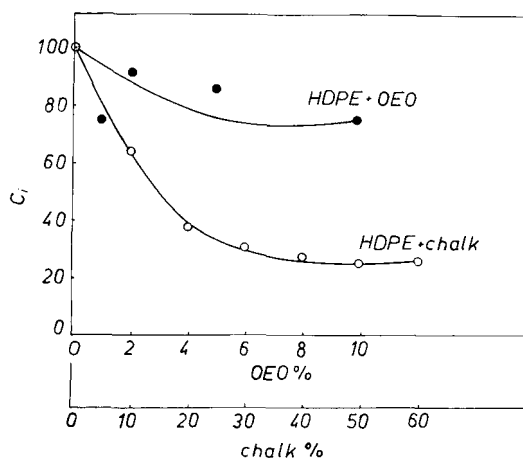


Fig. 7. Relative change of the impact strength of high-density polyethylene filled with unmodified chalk and with oligomer of ethylene oxide drawn against concentrations of chalk and of oligomer of ethylene oxide.

slightly decreases its tensile strength. The addition of OEO to HDPE up to 5% increases the elongation at break of the latter, and then it decreases if more OEO is added. This means that OEO alone does not act as a plasticizer for HDPE.

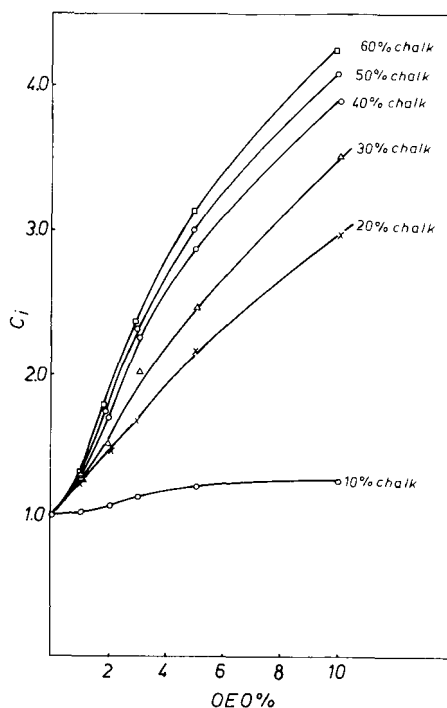


Fig. 8. The dependences of impact strength of high-density polyethylene filled with various amounts of chalk modified with oligomer of ethylene oxide on the concentration of oligomer of ethylene oxide. Each curve scaled to the value of the impact strength of the HDPE samples containing the respective percentage of unmodified chalk.

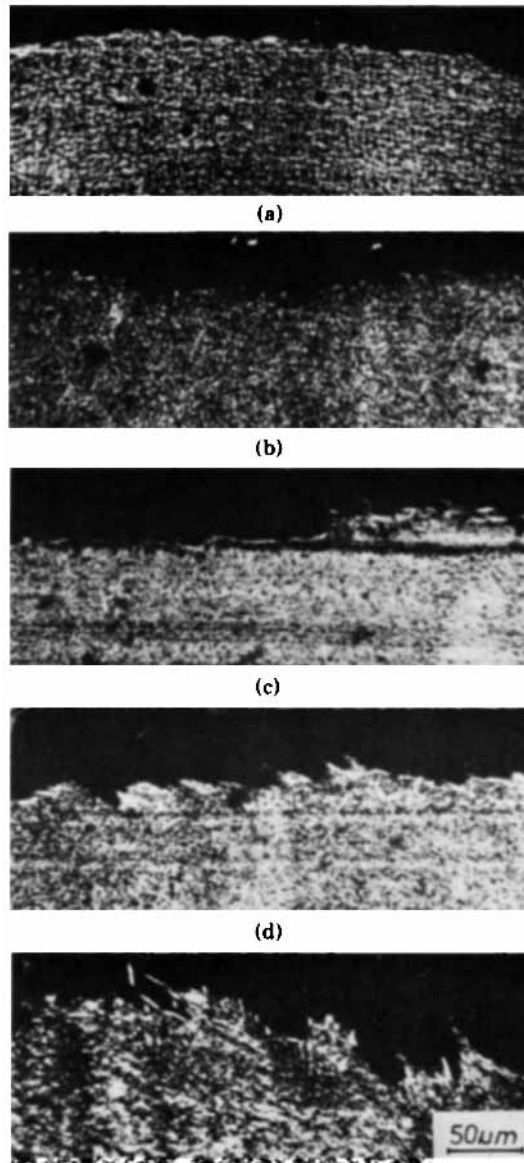


Fig. 9. The polarizing micrographs of thin sections cut perpendicularly to the fracture face of specimens after impact test of: (a) HDPE; (b) HDPE filled with 40% of chalk; (c) as above but 3% of OEO added; (d) as above but 10% of OEO; (e) as above but 20% of OEO added.

In Figures 4, 5, and 6, the graphical representation of the tensile properties of HDPE-modified chalk composites against OEO concentration are shown. It can be seen that there are sharp decreases in the modulus of elasticity and tensile strength of the HDPE-modified chalk composites. These decreases are great especially for low OEO concentrations for all compositions, and the relative values become more or less constant beyond 3% OEO. Table I shows the absolute values of the tension test data of HDPE—chalk (unmodified and modified). It can be

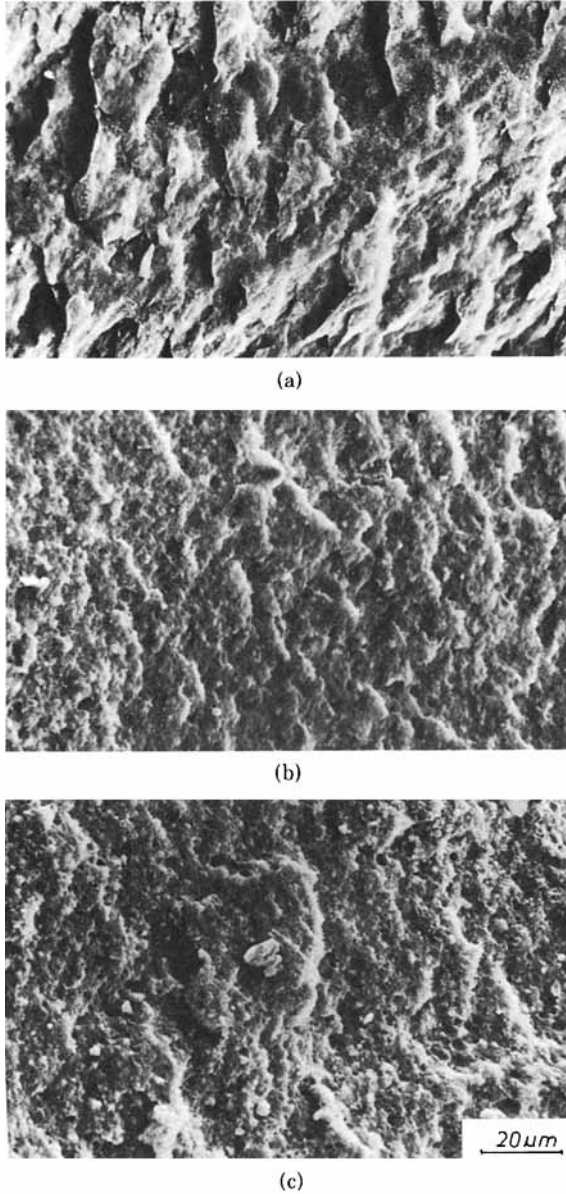


Fig. 10. The scanning electron micrographs of fracture surface of specimens after impact test: (a) HDPE; (b) HDPE filled with 40% of chalk; (c) HDPE filled with 40% of chalk modified by 10% of OEO.

seen from this table that the elastic modulus and tensile strength of HDPE filled with chalk modified with OEO in amounts larger than 3% are close to that of pure HDPE.

It is also seen that OEO increases the relative values of elongation at break of HDPE—chalk composites. This increase is very sharp for all HDPE filled with chalk containing 5% OEO or more. Table I shows that the absolute values of elongations at break for HDPE-modified chalk composites are always less than that of pure HDPE.

TABLE II
Impact Strength (J/m^2) of HDPE and HDPE-Chalk and HDPE-Modified Chalk Composites

OEO (%)	Chalk (%)				
	0%	10%	20%	30%	50%
0	4890	3130	1840	1530	1240
1.0	3170	3190	2200	2040	1830
2.0	4540	3350	2660	2220	2100
3.0	3260	3560	3040	3030	2850
5.0	4190	3770	3950	3670	3690
10.0	3700	3910	5440	5260	5080
20.0	—	—	11690	8560	6320

Thus it can be concluded that it is possible to prepare HDPE filled with modified chalk having more or less the same values of modulus of elasticity and tensile strength of pure HDPE but a higher ultimate strain than those composites containing unmodified chalk.

Figure 7 shows the effect of unmodified chalk and OEO additions on the impact strength of HDPE. Figure 7 indicates that the addition of unmodified chalk to HDPE sharply decreases its impact strength. For example, the addition of 20%, 30%, and 50% unmodified chalk to HDPE decreases the impact strength to 0.38, 0.31, and 0.25 of the initial value of HDPE, respectively. This means that HDPE unmodified chalk composites are less resistant to shocks. The same figure shows that the presence of OEO decreases the impact strength of HDPE but to small extent. For example, the addition of 2% and 5% OEO to HDPE decreases its impact strength to 0.93 and 0.86, respectively.

On the other hand, the addition of OEO to chalk improves the impact strength of its composites with HDPE, as seen from Figure 8. This figure shows that OEO improves greatly the impact strength of HDPE modified chalk composites, and this improvement goes hand in hand with the OEO concentration. Table II shows the absolute values of the impact strength of HDPE chalk unmodified and modified composites, and it is clear that the impact strength of all the composites of HDPE chalk containing 5% OEO are less than that of pure HDPE. The use of higher OEO concentration leads to higher impact strength. The micrographs of the fracture face profiles of HDPE and composites containing 40% of unmodified and modified chalk are presented in Figures 9(a)–9(e), respectively. The fracture faces of the same HDPE and compositions as seen in scanning electron microscope are shown in Figures 10(a)–10(c).

There is an apparent difference in fracture surface development of the samples. It shows that while the presence of chalk particles does not influence the fracture path in the polymer, the addition of OEO to the system improves it considerably. More careful examination of the fracture face profiles shows plastic deformation of pieces of the polymer sticking out from the surface of fracture. Polarizing microscopy of thin sections of composites containing more than 10% of chalk does not show any spherulitic structure of HDPE. The addition of OEO does not cause either any visible change of supermolecular structure of HDPE in thin section if chalk was etched by HCl. The degree of crystallinity in HDPE composites were possible to be determined by X-ray diffraction due to the fact that the main X-ray reflexes of the crystalline phase of HDPE are below $2\theta = 23^\circ$ while for chalk they were above 24° . The degrees of crystallinity of HDPE filled

with chalk are quite independent of OEO and chalk contents being in the range of 0.63–0.67.

The above observations indicate that the addition of OEO to the composites does not change the supermolecular structure and the degree of crystallinity of the polymer.

CONCLUSIONS

The presence of OEO in HDPE has an insignificant effect on the modulus, but it decreases the tensile and impact strengths, though slightly. On the other hand, while the addition of OEO up to 5% increases the elongation of high-density polyethylene, concentrations higher than 5% show reverse effect. These lead to the conclusion that ethylene oxide oligomer alone does not act as plasticizer for high-density polyethylene.

The composites prepared from high density polyethylene and 10–30% of chalk modified by 3–5% OEO have similar modulus of elasticity and tensile strength as pure high-density polyethylene and have quite high ultimate elongation and impact strength. High values of the ultimate elongation of HDPE filled with modified chalk indicate that the heterogeneity of the material caused by the chalk particles are not the origin of fracture of the samples. High values of the impact strength of these composites point out that the cracks generated in the impact tests are damped by the chalk particles modified with OEO. In the same tests the sample containing unmodified chalk show low ultimate elongation and impact strength.

From the microscopic observations it follows that the mechanical property change due to the introduction of OEO is not caused by the change of supermolecular structure of the polymer. The fracture paths exhibit significant development after introducing OEO to the system showing some plastic deformation near the fracture surface.

It can be concluded finally that OEO acts as an inhibitor of crack formation process, i.e., it dampens the generation and/or propagation of cracks; thus the plastic deformation of the polymer in the whole sample while elongated or in the layer near the fracture surface in impact test can be achieved.

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