

# Low-Density Polyethylene Filled with Chalk and Liquid Modifier

R. KALIŃSKI, A. GALESKI, and M. KRYSZEWSKI *Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90-362 Łódź, Poland*

## Synopsis

Based on the concept of introducing a liquid layer between the polymer and filler, a composition containing low-density polyethylene, chalk, and oligomer of ethylene oxide was proposed. Compositions containing up to 50% chalk modified with ethylene oxide exhibit typical thermoplastic behavior, i.e., neck formation and plastic deformation. They also show high-impact strength and other good properties. On the basis of mechanical data, the main action of the ethylene oxide oligomer in the system is to inhibit crack generation and propagation.

## INTRODUCTION

Thermoplastics are often filled with mineral fillers for the purpose of lowering costs or changing the mechanical properties. Usually, the modulus of the filled materials is strongly increased while the tenacity is decreased. For high degree of filling, the material cannot be processed since the viscosity is too high. In order to overcome these disadvantages, many methods have been developed based mainly on the phenomena occurring at the interface.<sup>1-16</sup> We suggested the application of the liquid layer between the polymer and filler.<sup>17</sup> The used liquid should permeate both the matrix and the filler. If the liquid layer around the filler particles is thick enough, the deformation can occur without losing the contact between filler and polymer. The liquid layer in such systems inhibits fracture phenomena, i.e., crack formation and propagation.

In the case of polypropylene filled with chalk, the most suitable layer is an oligomer of ethylene oxide. The composites of polypropylene containing up to 60% chalk by weight exhibit the properties of a thermoplastic material showing necking while being deformed. The impact strength is significantly improved compared to the unmodified composite and polypropylene. The tensile strength, however, is linearly decreased while the amount of chalk in the material is increased.

We now report studies of filling low-density polyethylene with chalk. Based on the idea of a liquid interface, an appropriate liquid for low-density polyethylene and chalk was sought. Composites containing various amounts of low-density polyethylene (LDPE), chalk, and liquids were investigated to discover the best thickness of the liquid layer and to determine compositions with optimal mechanical properties.

## EXPERIMENTAL

### Materials

Low-density polyethylene (Politen, Polish product), density 0.920 g/cm<sup>3</sup>, 30 CH<sub>3</sub> side groups per 1000 C in the main chain, microscopic melting point 107°C, was used.

Precipitated chalk of density 1.6–2.5 g/cm<sup>3</sup> (Polish product) was used. Chalk was characterized by particle size distribution (Table I).

Glycerin, ethylene glycol, and oligomer of ethylene oxide of molecular weight 200 were tested as liquid modifiers since they can survive the processing conditions.

### Sample Preparation

Chalk was covered with tested liquids in a thick water suspension, then the pulp was dried thoroughly at 120°C for 12 h. Modified chalk was mixed with low-density polyethylene by extrusion at 200°C. The extruder was equipped with a static mixer<sup>18,19</sup> at its orifice. Granulates of filled polyethylene were used for preparation of samples (films and thick sheets) by compression molding for further tests.

The supermolecular structure of 0.4-mm films was differentiated by two regimes of cooling: dipping molten films with chromium-plated brass covers in ice water (fast cooling) or cooling slowly in air (slow cooling).

### Methods

Oar-shaped samples were cut from films for Instron tensile tests. The deformation rate was 5%/min at 23°C. The impact strength was measured by the Charpy method using notched samples machined from 4-mm-thick sheets.

The density of the samples was measured by the floating method in a mixture of methanol and carbon tetrachloride at 23°C.

The viscosity of the samples was measured on an Instron capillary rheometer at 190°C introducing Rabinowitz and Bagley corrections.

The resistivity of samples to UV light in air was tested by means of tensile experiments conducted on 0.4-mm-thick films exposed to  $1.22 \times 10^{15}$  photons/

TABLE I  
Particle Size Distribution of Chalk<sup>a</sup>

Size, $\mu\text{m}$	Fraction, %	Size, $\mu\text{m}$	Fraction, %
2.5	15.44	13.75	0.54
5.0	20.32	15.0	4.33
6.25	7.18	16.25	0.13
7.5	15.98	17.5	1.49
8.75	5.15	18.75	0.27
10.0	15.85	20.0	0.67
11.25	1.76	21.25	0.13
12.5	9.48	22.50	1.08
		23.75	0.13

<sup>a</sup> Cylindrical shape of chalk particles was assumed. The thickness of the cylinder was 0.6  $\mu\text{m}$ , while the length was the size parameter, listed above.

TABLE II  
Tensile Parameters of LDPE Filled with Modified Chalk

Composite 7:3	Modulus, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	Tensile strength, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	Ultimate elongation, %
LDPE + chalk	125.5 ± 7.0	8.2 ± 0.1	105 ± 5
LDPE + chalk + glycerin	94.0 ± 2.0	8.4 ± 0.1	130 ± 30
LDPE + chalk + ethylene glycol	97.0 ± 2.0	8.6 ± 0.2	90 ± 10
LDPE + chalk + OEO	103.0 ± 3.0	8.6 ± 0.1	250 ± 35

sec/cm<sup>2</sup> high-pressure mercury UV light from a distance of 0.45 m for various periods of time. After a half-time, the reverse sides of the films were exposed to UV light.

The environmental effect was investigated during tensile tests in the presence of water, methanol, and motor oil at 23°C. The deformation rate was 100%/min.

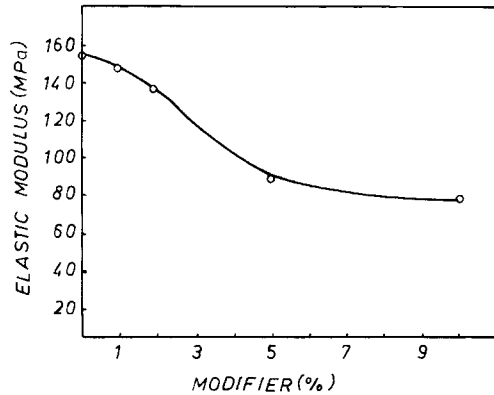
A fatigue experiment was also conducted for film samples followed by a tensile test. Fatigue testing consisted of 1000 cycles of deformation to 5% elongation at a rate of 50%/min and relaxation.

## RESULTS

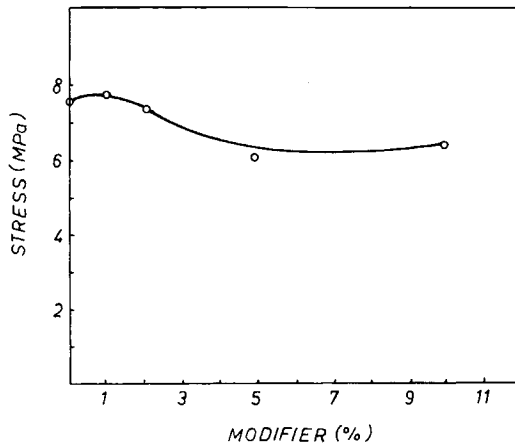
Four composites containing 70% LDPE and 30% chalk, 70% LDPE and 30% chalk modified with 1% glycerin, ethylene glycol, and oligomer of ethylene oxide (OEO) were prepared and tested in a tensile experiment. The results are shown in Table II. Glycerin and ethylene glycol decrease the modulus and do not practically change the tensile strength or ultimate elongation (Table II). Oligomer of ethylene oxide strongly improves the ultimate elongation of the material. The contact between filler and polymer is ensured via OEO adhered to both components. OEO evidently prevents the premature cracking of the samples. OEO was used for further modification of the system LDPE and chalk. The composites containing 50% LDPE and 50% modified chalk were used to determine the optimal amount of OEO in the system. The mechanical parameters characterizing the samples are shown in Figs. 1(a)–(d) as functions of the OEO contents. The decrease in elastic modulus, slow decrease in ultimate strength, linear increase in ultimate elongation, and strong increase in impact strength occur with increasing amounts of OEO in the composition. The optimal amount of OEO is 5 to 10% of the total amount of modified chalk by weight. This is a compromise between the decrease in elastic modulus and ultimate strength and increase in ultimate elongation and impact strength.

The 5 to 10% OEO content corresponds to a layer of OEO around each chalk particle 450 to 900 Å thick. Analogous mechanical parameters for the 5:5 compositions are shown in Table III for samples containing 60% LDPE and 40% modified chalk. Again, the optimal amount of OEO in the composition is 5 to 10% modified chalk by weight.

All modified samples (also for other amounts of chalk below 60% by weight) exhibit a stress–strain behavior typical of soft plastics. The samples undergo necking and flow during deformation. In the case of LDPE filled with unmodified chalk, an increase in elastic modulus occurs as expected for simple physical



(a)



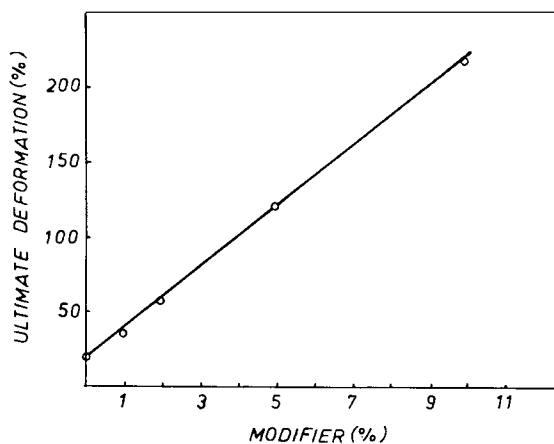
(b)

Fig. 1. Mechanical parameters of low-density polyethylene filled with chalk modified with various amounts of oligomer of ethylene oxide: (a) elastic modulus; (b) tensile strength; (c) ultimate deformation; (d) impact strength.

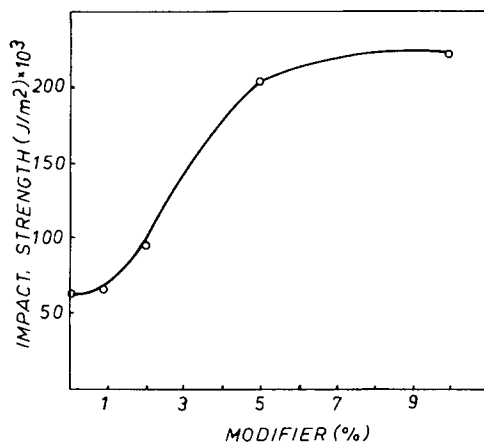
TABLE III  
Mechanical Parameters of LDPE Filled with Modified Chalk

Composition 6:4	Elastic modulus, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	Ultimate strength, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	Ultimate elongation, %	Impact strength, (J/m <sup>2</sup> ) × 10 <sup>3</sup>
LDPE + chalk	135.4	8.1	70	7.6
LDPE + chalk + 1% OEO	113.8	7.6	130	18.0
LDPE + chalk + 5% OEO	74.2	7.0	150	22.8
LDPE + chalk + 10% OEO	72.4	7.0	190	21.7

inclusion of chalk particles into LDPE. The samples containing chalk modified with oligomer of ethylene oxide exhibit a higher elastic modulus than the unfilled LDPE. However, the series of samples containing the same percentage of OEO with regard to chalk, but with various degrees of filling, exhibit small changes in elastic modulus. The samples filled with unmodified chalk show a dramatic



(c)



(d)

Fig. 1. (Continued from previous page.)

decrease in the ultimate elongation, while increasing the degree of filling. The addition of oligomer of ethylene oxide in 5–10% by weight significantly modifies the decrease. Samples containing 50% modified chalk can be deformed up to 200–250%. OEO has a very strong effect on the impact strength of the material. Small additions of OEO increase the impact strength by a factor of 3 to 4 for samples containing 50% modified chalk.

TABLE IV  
Density of the LDPE Filled with Modified Chalk

Composition	Density
LDPE	0.915
60% LDPE + 40% chalk + 5% OEO	1.22
60% LDPE + 40% chalk + 10% OEO	1.16
50% LDPE + 50% chalk + 5% OEO	1.33
50% LDPE + 50% chalk + 10% OEO	1.22

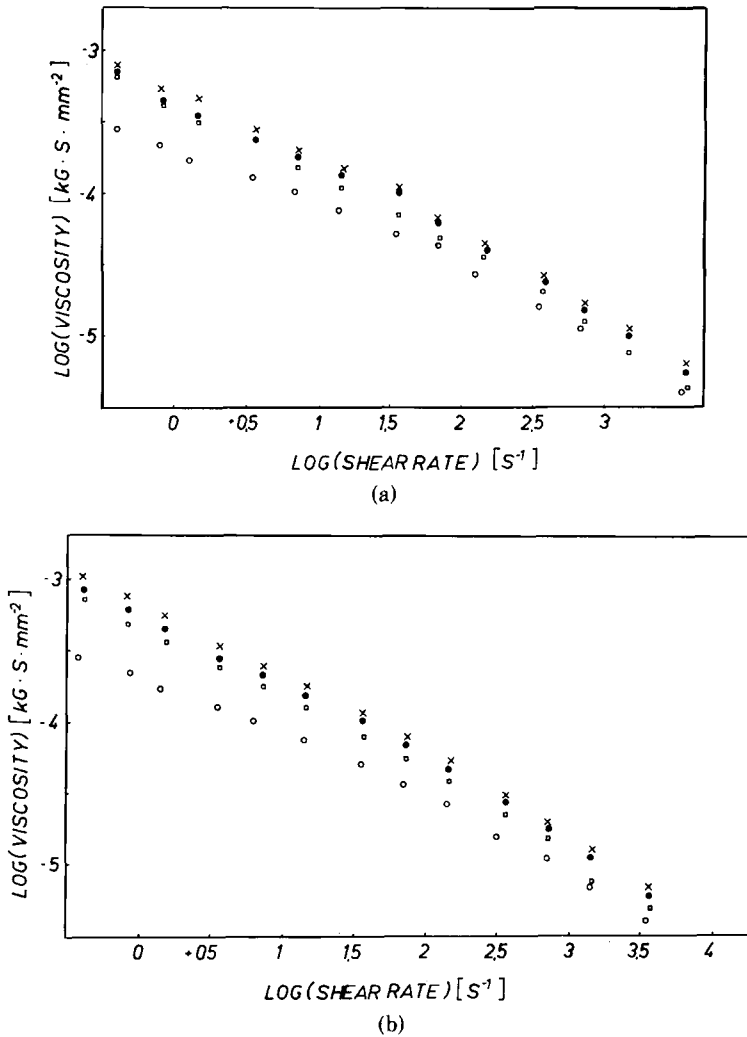


Fig. 2. Viscosity dependence of LDPE filled with modified chalk against shear rate: (a) curves for 60% LDPE + 40% modified chalk taken at 190°C; (b) curves for 50% LDPE + 50% modified chalk taken at 200°C. (○) LDPE, (×) LDPE + chalk, (●) LDPE + chalk + 5% OEO, (□) LDPE + chalk + 10% OEO.

### Density

The densities of the composites are given in Table IV. In the case of composites containing chalk with larger amounts of OEO, a decrease in the density is observed. The effect is due to the lower density of OEO (1.12 g/cm<sup>3</sup>) compared to the density of chalk (2.5 g/cm<sup>3</sup>).

### Viscosity

The dependence of viscosity of LDPE and several composites is plotted against shear rate in Fig. 2. All the curves for composites exhibit the same feature as the curve for LDPE. The viscosity of composites are two to three times higher

TABLE V  
Tensile Parameters of Composites Exposed to UV Light

Composition	Quality	0 h	10 h	50 h	90 h
60% LDPE + 40% chalk + 5% OEO	Modulus, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	74.2 ± 4.6	95.7 ± 2.0	94.4 ± 4.0	99.9 ± 3.5
	Elongation, %	150 ± 40	160 ± 40	125 ± 30	130 ± 30
60% LDPE + 40% chalk + 10% OEO	Modulus, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	72.4 ± 6.4	81.4 ± 10.0	83.4 ± 5.0	87.0 ± 2.0
	Elongation, %	180 ± 50	200 ± 30	230 ± 30	225 ± 45
50% LDPE ± 50% chalk + 5% OEO	Modulus, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	87.7 ± 4.0	100.8 ± 6.0	103.0 ± 1.0	116.7 ± 8.0
	Elongation, %	120 ± 25	100 ± 25	110 ± 45	110 ± 45
50% LDPE + 50% chalk + 10% OEO	Modulus, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	74.2 ± 6.0	90.1 ± 5.0	88.0 ± 4.0	88.1 ± 5.0
	Elongation, %	215 ± 10	175 ± 25	210 ± 30	200 ± 20

TABLE VI  
Tensile Parameters of LDPE Filled with Modified Chalk Cooled from Melt in Slow and Fast Regimes

Composition	Quality	Slow Cooling	Fast Cooling
60% LDPE + 40% chalk + 5% OEO	Modulus, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	115.9 ± 9.4	74.2 ± 4.5
	Tensile strength, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	7.2 ± 0.15	6.7 ± 0.6
	Elongation, %	95 ± 20	150 ± 40
60% LDPE + 40% chalk ± 10% OEO	Modulus, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	103.4 ± 3.5	72.4 ± 6
	Tensile strength, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	7.75 ± 0.2	7.0 ± 0.3
	Elongation, %	170 ± 55	180 ± 50
50% LDPE + 50% chalk + 5% OEO	Modulus, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	124.0 ± 58	87.7 ± 4.0
	Tensile strength, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	6.3 ± 0.1	6.0 ± 0.3
	Elongation, %	105 ± 10	120 ± 25
50% LDPE + 50% chalk + 10% OEO	Modulus, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	107.0 ± 5.0	72.4 ± 6.0
	Tensile strength, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	6.8 ± 0.3	6.5 ± 0.2
	Elongation, %	160 ± 45	215 ± 15

than the viscosity of LDPE. The addition of OEO decreases the viscosity significantly.

### Resistance to UV Light

The tensile parameters for the composites unexposed and exposed to UV light are presented in Table V. The UV light increases the modulus of the composites and does not change the ultimate elongation and tensile strength (not shown in Table V).

The increase in the modulus is likely due to some crosslinking which occurred at the interface chalk-liquid-polymer. However, prolonged exposition to the UV light does not destroy the samples, since the dose absorbed by the polymer is strongly reduced by a high amount of chalk.

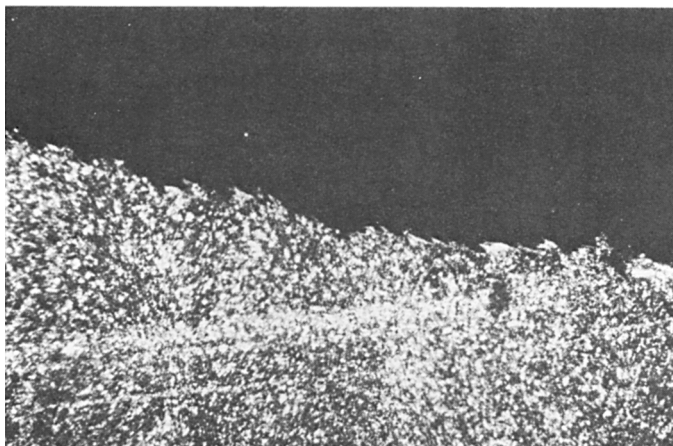
### Effect of Sample Preparation

The influence of the rate of cooling on the mechanical properties of composites is shown in Table VI. Slow cooling causes an increase in the elastic modulus and tensile strength and a decrease in the ultimate elongation of composite samples compared to "fast" cooled samples.

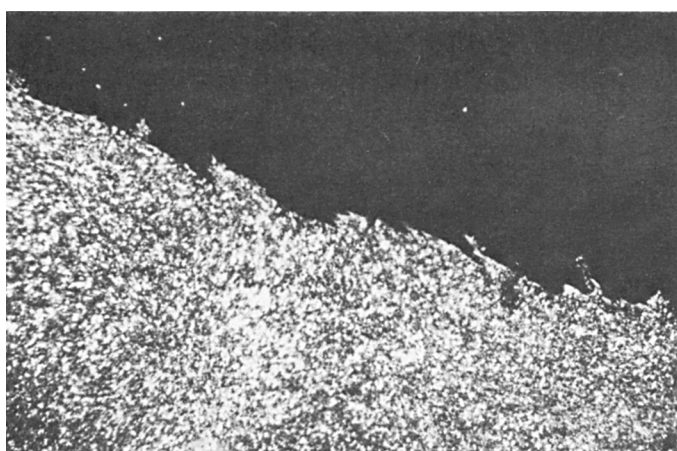
The changes are due to the change in supermolecular structure of LDPE in the composites. There are two additional factors: the change in heat conductivity due to chalk, and the presence of many interfaces (polymer-liquid-chalk) which influences the formation of a supermolecular structure of LDPE during cooling.

The interfaces act as nucleating agents. LDPE in compositions has no spherulitic structure. This was verified by small-angle light scattering patterns





(a)



(b)

Fig. 3. Thin slices cut across the fracture surface of low-density polyethylene filled with chalk; samples after the impact test: (a) sample containing 60% LDPE and 40% chalk by weight; (b) sample containing 60% LDPE and 40% chalk modified with 10% oligomer of ethylene oxide.

obtained from thin slices of compositions from which chalk was removed by hydrochloric acid.

### Environmental Effect

The tensile parameters of composites tested in the presence of air, water, methyl alcohol, and motor oil are presented in Table VII. Air, water, and methyl alcohol influence neither the tensile strength nor the ultimate elongation of composites. Motor oil decreases both quantities. The elastic modulus is not affected by air, water, methyl alcohol, or motor oil.

The environment does not cause the premature cracks in the initial region of the stress-strain curve. Motor oil introduces environmental cracks after the sample has formed the neck.

TABLE VII  
Effect of the Environment on the Tensile Parameters of Composites

Composition	Properties		Air	Water	Methyl alcohol	Motor oil
	Tensile strength, $(\text{N}/\text{m}^2) \times 10^6$	Elongation, %				
60% LDPE + 40% chalk + 5% OEO	Tensile strength, $(\text{N}/\text{m}^2) \times 10^6$		7.4 ± 0.2	7.5 ± 0.1	7.6 ± 0.2	7.2 ± 0.2
	Elongation, %		205 ± 50	110 ± 80	245 ± 20	95 ± 10
60% LDPE + 40% chalk + 10% OEO	Tensile strength, $(\text{N}/\text{m}^2) \times 10^6$		8.5 ± 0.2	8.7 ± 0.4	8.7 ± 0.3	7.5 ± 0.1
	Elongation, %		270 ± 60	350 ± 20	320 ± 30	200 ± 40
50% LDPE + 50% chalk + 5% OEO	Tensile strength, $(\text{N}/\text{m}^2) \times 10^6$		7.0 ± 0.2	6.8 ± 0.1	6.6 ± 0.2	6.0 ± 0.2
	Elongation, %		185 ± 30	200 ± 20	190 ± 10	95 ± 40
50% LDPE + 50% chalk + 10% OEO	Tensile strength, $(\text{N}/\text{m}^2) \times 10^6$		7.6 ± 0.2	7.8 ± 0.1	7.6 ± 0.2	7.2 ± 0.2
	Elongation, %		310 ± 20	330 ± 30	250 ± 30	195 ± 20

TABLE VIII  
Tensile Properties after the Fatigue Experiment

Composition	Properties	Before fatigue	After 1000 cycles
60% LDPE + 40% chalk + 5% OEO	Modulus, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	74.2	79.4
	Tensile strength, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	6.7	6.8
	Elongation, %	150	190
60% LDPE + 40% chalk + 10% OEO	Modulus, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	72.4	85.4
	Tensile strength, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	7.0	7.4
	Elongation, %	185	250
50% LDPE + 50% chalk + 5% OEO	Modulus, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	87.7	89.2
	Tensile strength, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	5.9	6.2
	Elongation, %	120	140
50% LDPE + 50% chalk + 10% OEO	Modulus, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	74.2	75.7
	Tensile strength, (N/m <sup>2</sup> ) × 10 <sup>6</sup>	6.5	6.8
	Elongation, %	215	230

### Fatigue Properties

Table VIII shows the tensile parameters of films pressed from the composites after a fatigue test. The fatigue test does not deteriorate the samples. In contrast, some increase in the elastic modulus, tensile strength, and ultimate elongation occurs for cyclic deformed samples. The liquid on the interfaces prevents cavitation which is normally formed in fatigue tests of unmodified compositions.

### DISCUSSION

The introduction of liquid OEO to the interface between the filler and polymer causes large changes in the ultimate mechanical parameters of the composites. All the samples containing filler covered with a liquid modifier exhibit typical stress-strain behavior for thermoplastics. The neck formation step follows the initial elastic region. The fracture occurs when the neck has covered the total length of the sample. The action of the OEO in the failure of the material could be of two kinds: the presence of liquid modifier could enlarge the fracture surface and/or it could inhibit crack initiation and propagation by the absorption of energy.

In Figs. 3(a) and (b), thin slices showing the surface of the fractured samples in the impact test are presented for unmodified and modified chalk in the composites, respectively. There is little surface development due to the addition of OEO which could be correlated with the three- to fourfold increase in the impact strength. Therefore, the liquid OEO inhibits crack initiation and propagation. It allows the composites to be deformed in the plastic region above 200% of elongation and highly increases the impact strength.

The independence of the elastic modulus of the composites containing the modified chalk on the degree of filling can be explained by an incomplete covering of the filler particles by OEO since direct contact increases the elastic modulus. The OEO reduces the thermal resistance on the polyethylene-chalk border. Due

to the higher heat conductivity of chalk, the heat can be effectively abstracted from the interior of the sample. Faster cooling can cause changes in the supermolecular structure of polyethylene leading to the stated effect on the elastic modulus.

The tensile strength of all the samples decreases with increasing amount of chalk. The modified and unmodified samples behave in the same way. In the samples without the OEO, the cavitation occurring during deformation causes the separation of the chalk surfaces from the polymer. The contact of the polymer with chalk is poor in deformed samples. The liquid modifier is also not able to transmit the quasistatic tensile stresses; thus, all the tensile forces in both cases are concentrated in the polymer matrix. Since the effective cross section of the polymer is the same in the samples containing unmodified and modified chalk, the tensile strengths are close. The effective cross section of the polymer in the composites decreases with increasing amount of chalk; the tensile strength decreases similarly. The main action, therefore, of a liquid in the system of filled polyethylene on the mechanical properties is to influence the generation and propagation of cracks.

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