

Modification of Properties of CaCO₃-Polymerization-Filled Polyethylene

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ABSTRACT: CaCO₃-polyethylene (PE) compositions, containing an ultrahigh molecular polyethylene (UHMPE) interlayer between the filler surface and the PE matrix, were synthesized by two-step polymerization of ethylene on a filler surface activated with a suitable catalyst. The properties of the compositions were studied depending on the molecular weight of the PE matrix and the thickness of the UHMPE intermediate layer at the filler particles. It was shown that the presence of UHMPE as an interlayer in chalk-UHMPE-PE compositions leads to an increase of plastic deformation of the materials as long as the M_w value of the PE matrix is higher than is the brittleness threshold for PE. Chalk-UHMPE-PE compositions exhibit a higher ability

for plastic deformation compared to chalk-PE compositions based on a PE matrix of a molecular weight equal to the molecular weight of the total polymer phase (UHMPE-PE) in the first case. There is no improvement of the mechanical properties when the UHMPE is dispersed in the compositions and not as an interlayer between a filler and a matrix. This means that the method of polymerization filling allows one to incorporate the polymer interlayer with a desired nature and properties between a filler surface and polymer matrix in filled polyolefin compositions. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 577–583, 2003

Key words: polyethylene (PE); mechanical properties

INTRODUCTION

It is known^{1–5} that the introduction of fillers into polyolefins can exert a negative influence on the deformational properties and strength of materials. One of the methods for improvement of certain mechanical properties is a surface treatment of fillers with special coating agents.^{4,5} The application of coating agents favors a more homogeneous distribution of filler particles in the polymer matrix and the improvement of their adhesive interaction. The coating agent really forms the transitional layer at the polymer–filler interface. The effect of the character of the polymer–filler surface interaction and of the interface properties on the mechanical properties of filled polymers was analyzed in many theoretical and experimental investigations.^{1–3} The method of polymerization filling,^{6–10} where a filler is introduced into polyolefins during the synthesis of the polymer matrix, gives the possibility to trace how the interlayer affects the properties of the filled polymer.

According to the method of polymerization filling, the polymer matrix is formed directly as a coating of

regulated thickness at filler particles by the polymerization of a monomer or mixture of monomers on the filler surface activated by a suitable catalyst. The most efficient way for application of the method is the introduction of fillers into ultrahigh molecular polymers, for example, into ultrahigh molecular weight polyethylene (UHMPE), obtaining very highly filled polymers with a filler content up to 96% wt with a very uniform distribution of filler particles in the polyolefin matrix.^{8,11} Besides this, the method allows one to prepare, by two-step sequential polymerization on the filler particles, a two-layer coating, in which each polymer layer may differ in the desired properties. This is a way to incorporate, between the filler surface and the polymer matrix, an intermediate polymer layer of a desired nature and properties and to affect the properties of the composition as a whole.

This work presents the results concerning the synthesis of CaCO₃-polyethylene (PE) compositions of a regulated molecular weight, containing a UHMPE interlayer located at the CaCO₃-PE interface, using the method of polymerization filling. The obtained compositions, constituted of chalk particles with a two-layer polymer (UHMPE-PE) coating, were synthesized in a two-stage process of ethylene polymerization on a chalk surface activated by a supported vanadium catalyst. The mechanical properties and rheological characteristics of the compositions were investigated as a function of the thickness of the

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UHMPE interlayer and the molecular weight of the PE matrix.

EXPERIMENTAL

Materials and general operations

CaCO₃ (Super-Pflex) was used as a filler. The chalk had a very narrow particle-size distribution (0.2–1.0 microns—not less than 90% wt) and an average particle size of 0.6 microns. For activation of the filler surface, vanadium tetrachloride ($T_b = 148.5^\circ\text{C}$) and triisobutylaluminum from Aldrich were applied. Ethylene and propylene were of polymerization-grade purity. Iso-hexane was dried on molecular sieves under Ar and distilled over sodium.

All polymerization experiments were carried out in a temperature-controlled 3-L stainless-steel reactor equipped with inlets for gases (argon, hydrogen, ethylene, propylene), an activated filler suspension and solvent, a mechanical stirrer, and a thermocouple. The reactor was also equipped with a device to take a sample of the reaction mixture from the reactor during the polymerization. This device allowed one to take a small sample of the chalk-PE composition from the reactor directly after the first stage of the process prior to the synthesis of the UHMPE interlayer. Analysis of this sample allows one to exactly know the M_w value and the content of the PE matrix in the final chalk-UHMPE-PE composition. The reactor was preliminary prepared for the polymerization runs by evacuation (70°C , 1 h), cooling, and subsequent filling with argon.

Activation of filler surface

For the activation of the filler surface with a supported catalyst, 30 g of chalk was placed in a 0.5-L flask equipped with a stirrer. A flask with chalk was evacuated at ambient temperature and filled with dried argon. Then, 0.2 L of dried iso-hexane was introduced. For activation of the chalk, VCl₄, in the amount of 1×10^{-4} mol, and Al iBu₃, in the amount of 8×10^{-3} mol, were added to the flask under stirring.

Polymerization procedure

The synthesis of a two-layer polymer coating at the filler surface was performed as follows: First, the layer of PE matrix of a desirable molecular mass at the filler particles was obtained. For this, a suspension of 30 g of chalk, activated by a catalyst as described above, in 0.2 L of iso-hexane was introduced into the reactor under argon and 0.6 L of iso-hexane was added. Then, H₂, in a calculated amount, was introduced while stirring. The amount of H₂ depended on the desired M_w value of the PE matrix. It was calculated according to the

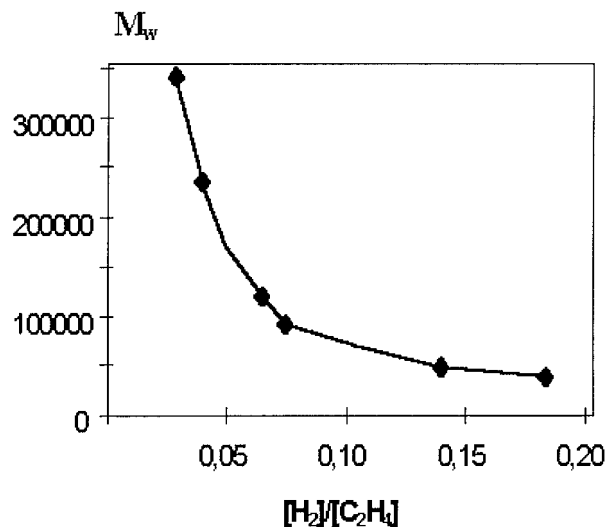


Figure 1 Dependence of HDPE molecular weight on $[\text{H}_2]/[\text{C}_2\text{H}_4]$ in ethylene polymerization on the chalk surface activated with a supported vanadium catalyst. Ethylene pressure: 4.5 atm; polymerization temperature: 70°C .

data of Figure 1, where the dependence of the M_w value on the $[\text{H}_2]/[\text{C}_2\text{H}_4]$ relation is shown. After this, the temperature was increased quickly to 70°C and ethylene was introduced. The polymerization was carried out at constant ethylene pressure of 4.5 atm and 70°C . After obtaining a certain amount of PE with the desired M_w value, the sample (in an amount of no more than 5 g) of the chalk-PE composition synthesized was taken from the reactor to evaluate the M_w value and the content of PE. The second stage of the process was a synthesis of UHMPE at the filler surface as an interlayer between the chalk surface and the PE coating, for which purpose the H₂ and ethylene mixture was removed from the reactor and replaced by pure ethylene. The ethylene polymerization was carried out at a monomer pressure of 2.4 atm and 70°C . Chalk-UHMPE-PE compositions containing the desired amount of UHMPE were obtained. Also, a run was made in which, in the second stage of the process, the ethylene-propylene copolymer was synthesized as an interlayer. For this, the ethylene-propylene (65.8% mol of C₃) mixture was introduced into the reactor after the removal of the H₂ and ethylene mixture. The copolymerization step was carried out at comonomer mixture pressure of 3.8 atm and 30°C . The polymerization was stopped with ethanol addition. The filled polymers were treated with ethanol once more and dried in a vacuum at 60°C . The products consisted of white powders.

Characterization of polymer compositions

For evaluation of the molecular mass characteristics of the matrix PE and the total polymer phase (PE

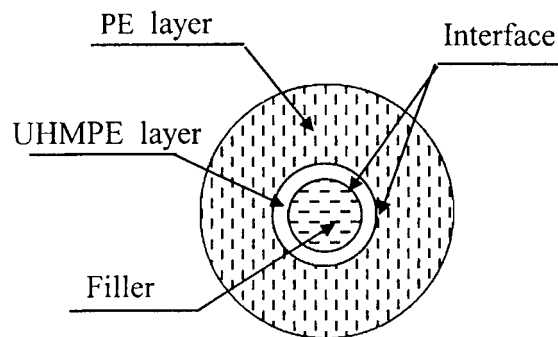


Figure 2 Schematical picture of chalk-UHMPE-PE composition particle obtained by polymerization filling.

+ UHMPE) in the compositions obtained, chalk was removed from the small samples of the chalk-PE and chalk-UHMPE-PE compositions by a treatment with HCl; then, the remaining polymer part was treated with H₂O and ethanol and dried at 60°C in a vacuum. The molecular masses of the polymers were measured by gel permeation chromatography (GPC) in *o*-dichlorobenzene at 140°C. The standard deviation of the M_w values measured was not higher than $\pm 10\%$. The melt-flow indexes (MIs) of the compositions were measured at 190°C under 2.16 and 21.6 kg loads (Russian GOST 11645, ASTM D 1238).

Mechanical tests of the compositions were performed using a JJ Instruments T5K tensile machine at ambient temperature and a deformation speed of 1 min⁻¹ (Russian GOST 11262 and 9550, ASTM D 638). Dumbbell samples were taken from plates of 1-mm thickness which were made by compression molding at 160°C and a pressure of 10 MPa. The dimensions of the samples for testing were as follows: length, 80 mm; equivalent length, 48.05 mm; width of the work part, 5 mm; and thickness, 1 mm (Russian GOST 11262). No fewer than seven samples were used for each test.

RESULTS AND DISCUSSION

With the method described above, a set of compositions based on chalk with a two-layer polymer coating, "chalk-UHMPE-PE," was obtained. UHMPE is located directly at the filler particle surface as a thin interlayer between the filler surface and the PE layer with a lower molecular mass (second layer). The second layer forms the polymer matrix in the composition after processing. This is schematically depicted in Figure 2. After processing, the second layer produces a continuous PE matrix of the sample with incorporated particles of the filler covered with a UHMPE layer. Obviously, both polymers (UHMPE and PE) overlap at the layer boundary with mutual penetration but with retention of the UHMPE coating at the particle surface. The probable reason for retention of the UHMPE coating at the surface of the filler particles after processing is the presence of an intimate physical interaction of the formed macromolecules with the filler surface (mechanical component of the adhesion) as a result of their synthesis directly on the filler surface.⁸ The fact that UHMPE has a very low flow during processing compared to PE obtained as a matrix in the polymerization-filled compositions is an additional reason for the retention of the UHMPE interlayer in the final composition.

The thickness of the UHMPE interlayer is varied by varying the UHMPE content in the range of (1.8 – 12) $\pm 0.2\%$ wt. The content of chalk in the compositions was kept at about 30 $\pm 0.5\%$ wt. The molecular mass of the second (PE matrix) layer in a set was 235,000. The mechanical properties of the materials obtained were measured. The results are given in Table I (runs 1.1–1.5).

The data of Table I show that the introduction of the UHMPE layer into the chalk-PE composition in the course of the two-step synthesis is accompanied by

TABLE I
Influence of UHMPE Interlayer Thickness in Chalk-UHMPE-PE Compositions on Their Mechanical Properties

No.	Composition	Filler content (% wt)	UHMPE content (% wt)		$M_w \times 10^{-3}$	M_w/M_n	E (GPa)	σ_y (MPa)	σ_t (MPa)	et (%)
			In total composition	In polymer coating						
1.1	Chalk-PE	25	0	0	235	6.5	1.1 \pm 0.03	28 \pm 0.5	22 \pm 0.3	90 \pm 20
1.2	Chalk-UHMPE-PE	29	1.8	2.5	260	8	1.1 \pm 0.08	27 \pm 0.9	21 \pm 0.6	140 \pm 30
1.3	Chalk-UHMPE-PE	30	4.9	7	320	9	1.1 \pm 0.03	25 \pm 0.3	33 \pm 2.0	460 \pm 40
1.4	Chalk-UHMPE-PE	31	6.4	10	360	13	1.1 \pm 0.04	25 \pm 0.3	27 \pm 2.0	420 \pm 40
1.5	Chalk-UHMPE-PE	31	12	17	500	13	1.1 \pm 0.04	26 \pm 0.4	23 \pm 3.0	320 \pm 40
1.6	Chalk-UHMPE	40	60	60	1600	8.5	1.1 \pm 0.03	19 \pm 0.4	23 \pm 1.4	170 \pm 10
1.7	Chalk-UHMPE	60	40	40	1600	8.5	1.4 \pm 0.09	17 \pm 0.6	22 \pm 2.0	160 \pm 10
1.8 ^a	Chalk-PE-UHMPE	31	3.2	4.6	250	11	1.4 \pm 0.05	26 \pm 0.3	21 \pm 0.6	50 \pm 20
1.9 ^b	Chalk-CEP-PE	25	7	10	290	9.3	1.0 \pm 0.05	30 \pm 0.8	24 \pm 1.0	40 \pm 10

^a The sample was synthesized with the reverse sequence of polymer layers on the filler surface: The first layer arranged directly on the chalk surface, is the PE layer, and the second one, located next is the thin UHMPE layer.

^b The CEP (propylene content in the copolymer was 28% mol) was synthesized as an interlayer in composition.

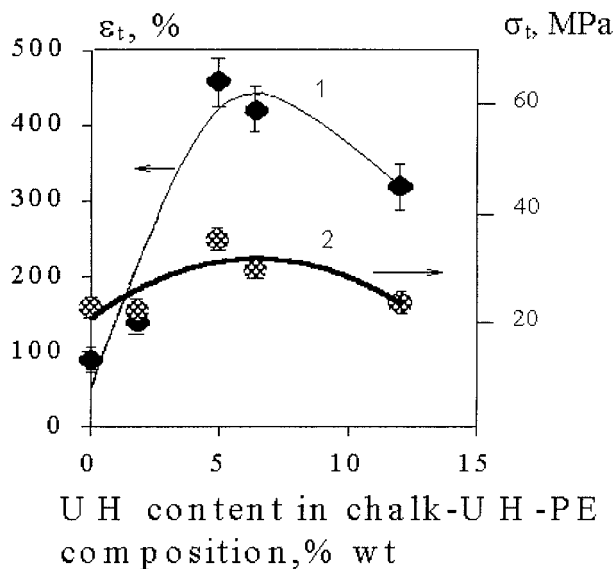


Figure 3 Influence of UHMPE interlayer thickness on (1) elongation and (2) tensile strength for chalk-UHMPE-PE compositions. Filler content in the compositions: 30% wt; M_w of PE matrix: 235,000.

some increase in the M_w value and polydispersity (M_w/M_n) of the total polymer coating. As may be seen from the results obtained, the UHMPE presence as an intermediate layer between the surface of filler particles and PE matrix leads to an increase of the elongation at break of the materials in all presented cases (Table I, runs 1.2–1.5) as compared to the chalk-PE composition (run 1.1). The reasons for the UHMPE interlayer effect on the mechanical properties of the filled UHMPE are discussed below.

The thickness of the UHMPE intermediate layer in compositions affects, essentially, both the ultimate elongation and tensile strength values, that is, the dependencies of the tensile strength and elongation at break on the UHMPE interlayer thickness passing through a maximum (Fig. 3). The maximum values of the characteristics are achieved at a UHMPE layer thickness of about 5–6% wt. For such compositions, the values of the elongation at break and tensile strength are equal to 420–460% and 27–33 MPa, respectively, which are essentially higher than for the composition without the UHMPE interlayer (run 1.1). The reasons for the UHMPE interlayer influence on the mechanical properties of the filled HDPE are discussed below.

Also, a composition with the reverse sequence of polymer layers on the filler surface was synthesized: The first one, arranged directly on the chalk surface, was the PE matrix layer, and the second one, located on top of it, was the thin UHMPE layer. The properties of such materials are shown in Table I (run 1.8). In this case, the introduction of UHMPE into the composition does not improve the properties of the filled compo-

TABLE II
Properties of Chalk-UHMPE-PE Compositions Depending on Molecular Weight of PE Matrix

No.	Composition	Filler content (% wt)	UHMPE content (% wt)		$M_w \times 10^{-3}$ (g/mol)	M_w/M_n	E (GPa)	σ_y (MPa)	ϵ_y (%)	σ_t (MPa)	ϵ_t (%)	ML, g/10 min at 190°C and load	
			In total composition	In polymer coating								2.16 kg	21.6 kg
2.1	Chalk-UHMPE-PE ($M_w = 40,000$)	33.7	3.6	5.5	120	8.5	1.4 ± 0.04	—	—	26 ± 0.4	2 ± 0.2	0.18	50
2.2	Chalk-UHMPE-PE ($M_w = 100,000$)	29	1.4	2	129	9	1.2 ± 0.04	28 ± 0.5	5 ± 0.2	21 ± 0.6	45 ± 10	0.06	6.7
2.3	Chalk-PE ($M_w = 120,000$)	28	0	0	120	6	1.2 ± 0.04	—	—	28 ± 0.3	5 ± 0.3	—	6

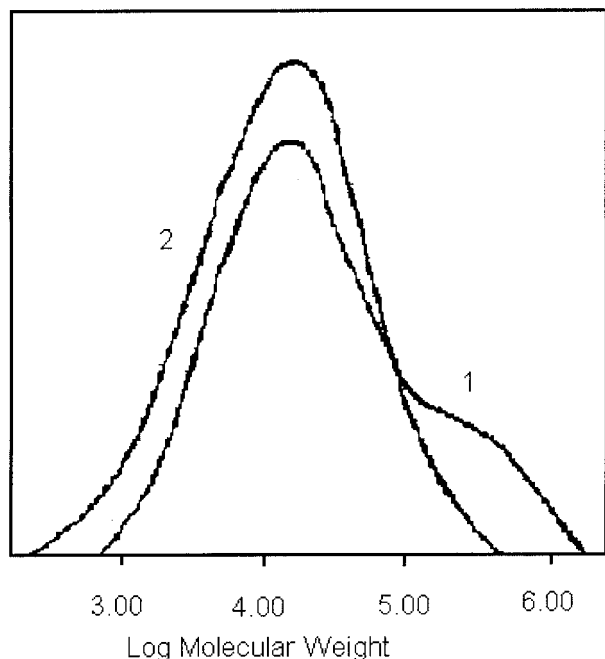


Figure 4 MWD curves (curve 1) of the total polymer phase from the chalk-UHMPE-PE sample and (curve 2) of the polymer phase from the chalk-PE sample. Both samples have the same PE matrix ($M_w = 40,000$).

sition. At the same time, this fact is circumstantial evidence that, in the compositions, where UHMPE was synthesized directly on the filler surface, UHMPE is retained as an interlayer between the filler and the PE matrix after processing. This means that only the UHMPE incorporation as an interlayer between filler and PE matrix allows one to improve significantly the plasticity and strength of the filled polyethylene. Otherwise, the introduced UHMPE can be considered merely as an additional filler, resulting in some decrease of the elongation at break and tensile strength.

Chalk-PE and chalk-UHMPE-PE compositions of a lower molecular weight PE matrix were also synthesized. The results are given in Table II. Here, the composition 2.1 contains a UHMPE interlayer (3.6% wt in composition) and a PE matrix with an M_w of 40,000. Composition 2.2 also contains a UHMPE interlayer (1.4% wt in composition) and has a PE matrix with an M_w of 100,000. The M_w of the total polymer coatings in these compositions are practically equal and are 120,000 and 129,000, respectively. Composition 2.3, in which the UHMPE interlayer is absent, has a PE matrix of the same M_w .

The increase of M_w and the broadening of the molecular weight distribution (MWD) of the coating polymer after incorporation of the UHMPE interlayer for a set of compositions with low M_w of the PE matrix are clear from the GPC data. As an example, the MWD for sample 2.1 and a sample without the UHMPE interlayer are given in Figure 4. The data show that, in

sample 2.1, two different polymers are present: Curve 1 (sample 2.1) has a shoulder in the region of high molecular weight which is absent in the case of the composition with a matrix of the same M_w value (40,000) but without the UHMPE interlayer (curve 2).

The data show that the modification of filled PE properties by incorporation of the UHMPE interlayer is not just the simple consequence of the increase in molecular weight of total polymer phase. Sample 2.3 does not contain a UHMPE layer and fails in a brittle manner, whereas sample 2.2, with the same M_w value of the total polymer phase but containing a UHMPE interlayer, shows the remarkable ability for plastic deformation. Besides, it is worth noting that the introduction of a thick UHMPE interlayer allows one to avoid the embrittlement of sample 2.2, in which the M_w of the PE matrix is even slightly lower than in the brittle sample 2.3. On the other hand, a too strong decrease of the polymer matrix M_w (run 2.1) leads to a high brittleness of the filled materials, that even incorporation of a thin UHMPE interlayer does not improve the plastic properties of the filled PE.

It is well known that the molecular weight of HDPE and the supermolecular structure—the content of crystalline and amorphous phases, the entanglement of macromolecules in amorphous regions, and the amount of connecting chains—are the controlling factors for the mechanical properties.^{12–15} HDPE of very low molecular weight fails in a brittle fashion with small elongation before necking. The threshold of brittleness for unfilled PE lies in the region of $M_w = 50,000$.¹² With an increase of M_w above the brittleness threshold, the straining of the polymer is accompanied by yielding and of clearly defined necking and by an increase of the elongation at break. However, the introduction of a filler into PE leads to the embrittlement of the material even at a significantly higher molecular weight of PE than the critical value mentioned above. This was also demonstrated by the data obtained (Table II, runs 2.1 and 2.3).

UHMPE, itself, combines the clearly defined high elastic properties with some plasticity. The UHMPE structure is characterized by small crystallites and the physical entanglement of the macromolecules in amorphous regions.^{12,15} The distinctive feature of UHMPE is the absence of yielding and necking during elongation, high tensile strength, and elongation at break of about 200–400%. UHMPE has large reversible deformations: The samples shrink 1.5–2 times after elongation. With introduction of a filler into UHMPE by the method of polymerization filling, compositions with a unique set of physical and mechanical properties are obtained.⁸ By virtue of the uniform distribution of the filler particles in the UHMPE matrix, the filled UHMPE preserves the properties of UHMPE and improves some properties. The chalk-UHMPE compositions preserve the ability for plastic

deformation and tensile strength on a reasonably high level with a chalk content up to 60% wt, as evident from Table I (runs 1.7, 1.8).

Owing to such properties, the UHMPE layer at the filler particle surface, incorporated between a filler and the PE matrix, inhibits, obviously, the propagation of cracks during deformation¹⁶ and improves the plasticity and strength of filled PE. The preparation of such compositions directly during the two-step polymerization process by sequential synthesis of UHMPE and PE on the same active sites ensures a good compatibility (on a molecular level) of the two polymers at the UHMPE-PE boundary and homogeneous distribution of chalk-UHMPE in the PE matrix after processing. At the same time, the molecular weight of the PE matrix is of great significance: As indicated above, the incorporation of UHMPE as an interlayer in chalk-UHMPE-PE compositions gives an improvement of the plastic properties of the materials if the M_w value of the PE matrix is higher than is the brittleness threshold for PE.

Notice that the mechanical blending of PE with the UHMPE-coated filler, in which the UHMPE coating is obtained also by ethylene polymerization at the filler surface, gives brittle materials¹⁷ in contrast to the two-layer compositions described above. In the case of mechanical blending, the required degree of homogeneity of filled compositions is not reached.

Taking into account the preceding, it is possible that, at the first stage (up to the yield point), the staining is defined mainly by the properties of the matrix. Then, at the second stage, the UHMPE layer and its amount affect the tensile strength and elongation at break. The thicker layer of UHMPE (to 5–6% wt) in the composition provides higher plasticity and tensile strength.

Even though the compositions 2.1–2.3 are characterized by similar M_w values of the total polymer phase (about 120,000) and a similar content of the filler, they have a significantly different MI, as is seen in Table II, where the MIs are given. At the same time, the molecular weight of the matrix polymer part in the compositions increases from 40,000 to 120,000. The MI of the compositions changes from 50 to 6 g/10 min at a load of 21.6 kg. The results allow one to conclude that the molecular weight of the matrix polymer controls the flow of these compositions. The incorporation of a small amount of UHMPE in the form of an interlayer increases the molecular weight of the total polymer part in the compositions and decreases the melt flow but is not the determining factor for the melt flow of the filled compositions (Table II).

The two-layer composition 2.2 containing 29% wt of chalk, the PE matrix with $M_w = 100,000$, and an intermediate UHMPE layer in an amount of 1.4% wt exhibits an interesting combination of properties: It com-

bines reasonably good tensile strength and an ability for plastic deformation with the ability to flow. The MI value for this material is 6.7 g/10 min at load of 21.6 kg and 0.06 g/10 min at load of 2.16 kg.

As an interlayer in the chalk-PE composition, an ethylene-propylene copolymer (CEP) was also synthesized instead of UHMPE (Table I, run 1.9). The propylene content in the copolymer was 28% mol. The content of the copolymer in the composition constituted 7% wt, and the PE matrix had a molecular weight M_w of 200,000. As evident from Table I, the sample with an interlayer of CEP of the used composition did not give as good a result as did UHMPE.

CONCLUSIONS

The method of polymerization filling allows one to incorporate a polymer interlayer of a desired nature and properties between the filler surface and the polymer matrix in filled polyolefin compositions by two-step polymerization on a filler surface activated by a suitable catalyst. The properties of such compositions based on PE and chalk were studied depending on the molecular weight of the PE matrix and the nature and thickness of the intermediate layer at the filler particles. The results show that the presence of UHMPE as an interlayer in the chalk-UHMPE-PE compositions led to an improvement of the plastic deformation of the materials if the M_w value of the PE matrix was higher than was the brittleness threshold for PE. The chalk-UHMPE-PE composition containing a UHMPE interlayer exhibits a higher ability for plastic deformation compared to the chalk-PE composition based on the PE matrix of a molecular weight equal to the molecular weight of the total polymer phase (UHMPE-PE) in the first layer. There is no improvement of the mechanical properties in the case where UHMPE is dispersed in the matrix. It is worthwhile investigating the effect of the CEP of a suitable composition as an interlayer in filled PE.

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