

Ludwik DOMKA^{*}, Andrzej WAŚICKI^{**}, Maciej KOZAK^{***}

THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF NEW HDPE-CHALK COMPOSITES

Received March 2003, reviewed, and accepted May 15, 2003

Increasing demands on the quality and specific properties of polymers imply increasing demands on the mineral fillers used in composite materials. They are expected not only to reduce the cost of production but also improve the mechanical properties of the composites or endow them with new features, e.g. thermostability. The paper presents a method for obtaining polyethylene composites with chalk modified by two new 1-alcoxymethyl-3-hydroxypyridinium chlorides: 3-hydroxy-1-octyloxymethylpyridinium chloride (salt 1) and 3-hydroxy-1-octadecyloxymethylpyridinium chloride (salt 2) and gives a characterisation of the composites obtained. Introduction of chalk modified with ammonium salts results in an increased values of MFI of the composites. The MFI changes are the most pronounced for the PE composites containing the filler in concentrations from 0.05 to 2.0% wt. Addition of the chalk modified with the ammonia salts causes greater changes in some mechanical properties of the composites (Young modulus) than addition of unmodified chalk, while changes in some other properties (stress at break) was practically the same.

Key words: chalk, surface modification, quaternary ammonium salts, polyethylene

INTRODUCTION

Mineral fillers used in polymer industry should be chemically inert towards the polymer matrix and components. They should show thermostability and ability to easy and fast dispersion in a polymer medium (Plueddemmann, 1974). The problem is that commonly used mineral fillers have hydrophilous surface while that of polymers is usually hydrophobic. Therefore, to improve the interphase interactions in a composite

^{*} Technological Centre, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland.

^{**} Department of Polymer Technology, Technical and Agricultural Academy of Bydgoszcz, Seminaryjna 3 85-326 Bydgoszcz, Poland.

^{***} Department of Macromolecular Physics, A. Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland, mkozak@amu.edu.pl.

a hydrophobisation of the filler surface is necessary (Domka, 1994). It is achieved with the use of proadhesive compounds such as organic acids and their derivatives, polyoxyethylene glycols, silane coupling agents or some surfactants like quaternary ammonium salts (Mittal, 1992; Domka et al., 2002a, 2002b). The later are particularly valuable because of bacterio- and fungistatic properties. The modified calcium carbonates are particularly suitable as fillers of the PE-LD and PE-LLD foils, containing up to 40% of carbonates. The foils have been commonly used in packaging thanks to their high mechanical strength and easy acceptance of print. The paper presents results of analysis of microstructure and mechanical properties of polyethylene composites filled with chalk modified with the two 1-alkoxymethyl-3-hydroxypyridinium chlorides substituted with C_8H_{17} or $C_{18}H_{37}$: 3-hydroxy-1-octyloxymethylpyridinium chloride (salt 1) and 3-hydroxy-1-octadecyloxymethylpyridinium chloride (salt 2).

MATERIALS AND METHODS

Chalk used in the study originated from the Sobków deposit. Chemical composition of the chalk included $CaCO_3$ (96.8%), Fe (0.033%), Mn (0.020%), H_2O (0.15%), Cu (traces) and insoluble residue (0.70%). The chalk manifested density of 2.59 g/cm^3 , specific surface area of $8.6\text{ m}^2/\text{g}$, bulk density of 336 g/dm^3 , crystallographic structure of calcite. For modification of chalk, two newly synthesized quaternary 1-alkoxymethyl-3-hydroxypyridinium chlorides were used. The modification process was described in our previous work (Domka et al, 1983, 2002b)

The composites were made with high density polyethylene (HDPE) Stavrolen 276-73, made in Russia. The samples to be studied were mixtures of the polyethylene with the chalk modified with quaternary ammonium salts with aliphatic substituents C_8H_{17} and $C_{18}H_{37}$. The modified chalk was introduced into HDPE in the amounts of 10, 5, 2, 1, 0.5, 0.1 and 0.05% wt. The mixtures containing from 1 to 10% wt of chalk were obtained by introducing appropriately weighted portions of chalk into molten polymer. The mixtures containing 0.05 to 0.5% of chalk were obtained by diluting earlier prepared concentrations containing a proper weight percent of chalk with polyethylene. The mixtures were homogenised in a Brabender plastograph with a measuring head of 50 g in capacity. The head was heated to about $150\text{ }^\circ\text{C}$ and the plasticised polyethylene chalk powder or concentration were added in small portions. After addition of each portion the mixtures were stirred for 20 minutes. After homogenisation the hot samples were removed from the head chamber and divided into three portions. The portions were pressed by a hydraulic press PHM-63 between two steel plates and anti-adhesive layers made of enforced teflon foil. The pressing was performed at $220\text{ }^\circ\text{C}$ under pressure increased to 15 MPa for 30 minutes. To obtain the foils, during the first 5 minutes the samples were heated between the plates not fully closed, for the next 5 minutes with the plates closed but under normal pressure, then for 15 minutes under pressure gradually increasing to 15 MPa. After

removal of the steel plates the pressed foils between the Teflon foil layers were cooled to ambient temperature. Then the Teflon foil was removed, the polyethylene foil samples in the form of oars were cut out, the shape B according to the standard ISO 3167-1996. The oar-shaped samples were used for the measurements estimating the strength of the foils, flow rate, and morphology of the hypermolecular aggregations.

SCANNING ELECTRON MICROSCOPY

The surface and cross sections of the composites were observed under SEM. To be able to do this the samples were sputtered with gold in an ionising sputtering chamber. Observations were made under a SEM -515 (Philips) at the exciting voltage of 20 kV.

STRENGTH MEASUREMENTS

The oar-shaped samples were subjected to strength determinations with a TIRA Test 2200. For determinations of the Young modulus the samples were stretched at the rate 1 mm/ min, for determinations of the bulk modulus of elasticity - at the rate of 20 mm/min (ISO 1133-1991).

RESULTS AND DISCUSSION

SEM photographs of the composites filled with the unmodified and appropriately modified chalk are presented in Figs 1 and 2. The influence of the modification on the tendency to agglomeration and aggregation of the fillers in the polymer matrix is apparent.

After the modification the fillers are capable of uniform dispersion in the matrix. This effect is definitely more pronounced for the chalk modified with salt 1. As a result of both types of modification the filler grains do not agglomerate. The mean size of the filler particles after the two modifications is similar.

For the samples containing 10% wt. of chalk with salts 1 and 2 the results were similar, Fig. 3. For these samples MFI was close to 1g/10 min, at the pressure on the piston of 35 N. With decreasing content of the chalk in PE the value of MFI increases, especially for the chalk concentrations of 0.1 and 0.05%. However, this increase is much lower than for unmodified chalk. The presence of chalk considerably decreases the MFI value (Fig. 4), and the presence of salt 2 containing a greater aliphatic substituent decreases it to a greater degree.

The Young modulus: its value depends on the type of chalk used. The smallest modulus have the samples with unmodified chalk (Fig. 5). The value of the modulus also depends on the concentration of chalk reaching the highest values for the chalk concentrations of 10 and 0.1% wt.

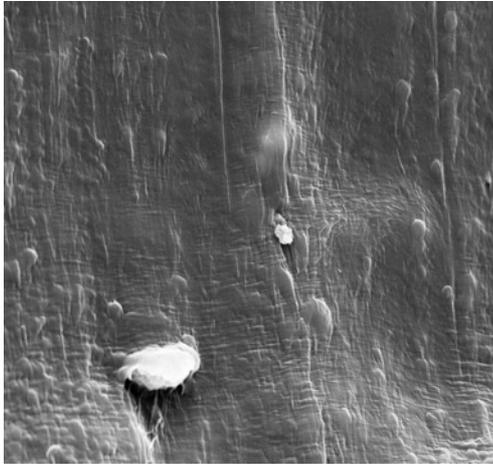


Fig. 1. SEM micrograph of HDPE filled with 20% unmodified chalk

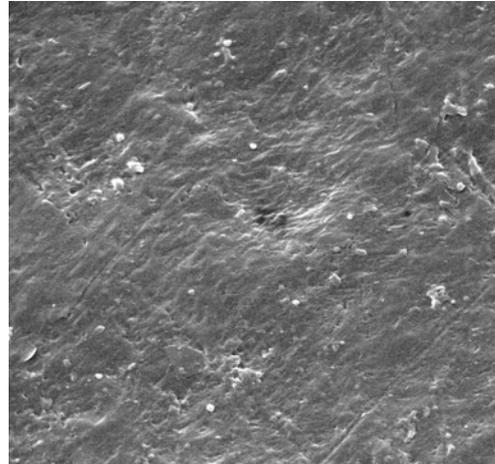


Fig. 2. SEM micrograph of HDPE filled with 20% chalk modified with salt 1

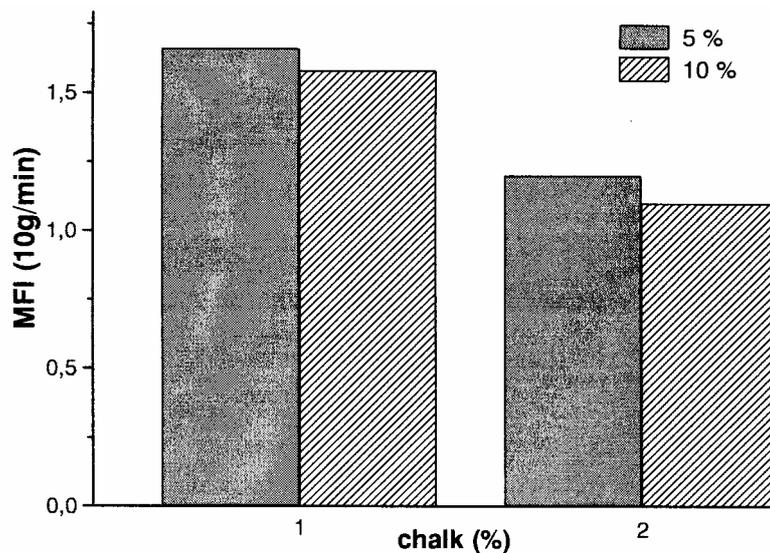


Fig. 3. Changes in MFI (melt flow index) of the PE samples with 5 and 10% wt of: chalk modified with ammonium salt 1 (1), chalk modified with ammonium salt 2 (2). Results obtained under the piston pressure of 35N

The increased value of the modulus for the sample with 0.1%wt chalk can be related to changes in PE crystallisation, although it has not been confirmed by other methods. The samples of PE modified with chalk and salt 1 with a shorter hydrocarbon substituent are characterised by higher modulus than those modified with chalk and salt 2, which means that the use of a properly selected substituent can have stabilising effect on the modified polymer.

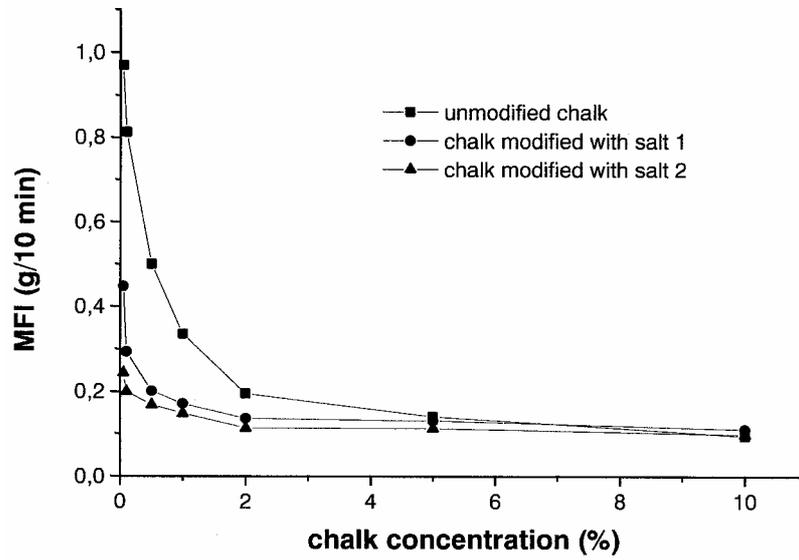


Fig. 4. Changes in MFI (melt flow index) of the PE samples with 0.05 - 10% wt of unmodified chalk or chalk modified with salt 1 and chalk modified with salt 2. Results obtained under the piston pressure of 35 N

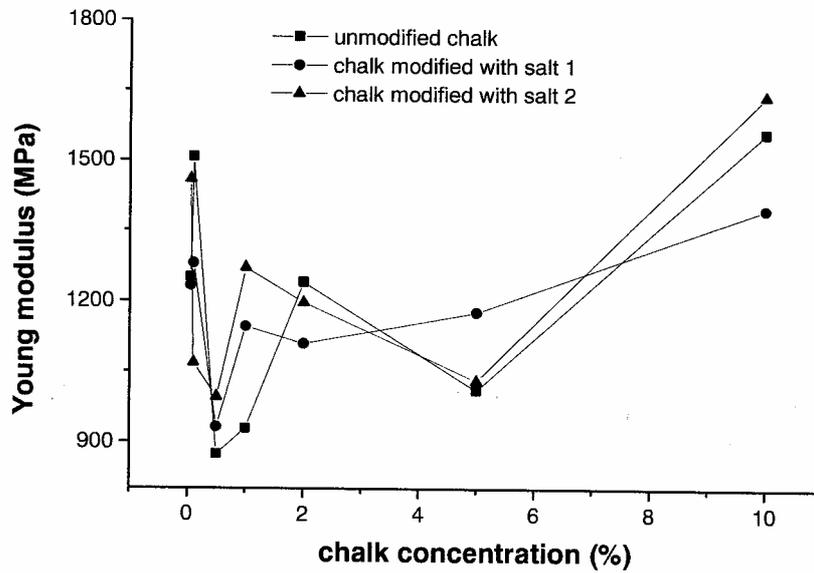


Fig. 5. The effect of the chalk additions on the Young modulus of HDPE composites with unmodified chalk, chalk modified with salt 1 and chalk modified with salt 2

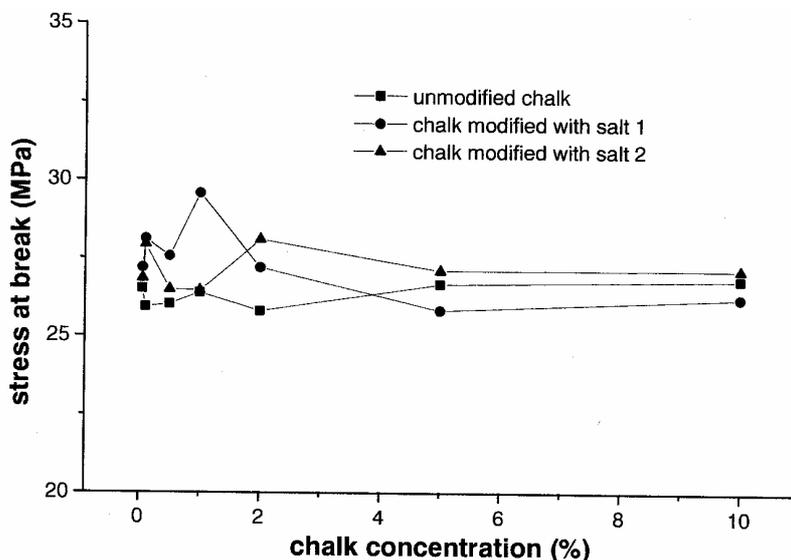


Fig. 6. The effect of chalk addition on the stress at break of HDPE composites with unmodified chalk, chalk modified with salt 1 and chalk modified with salt 2

The values of stress at break (Fig. 6) were practically the same for all samples, which means that the effect of the modifier on this parameter is negligible.

Similar influence of the chalk and coupling agents on the mechanical properties of composites has been recently observed. For titanates used as a coupling agents in PP/HDPE/CaCO₃ composites (Gonzales et al, 2002) an increase was verified in Young's modulus at 0.7 wt.% and in elongation at break (up to 0.7 wt.%). The values of the tensile stress and the complex melt viscosity of polyethylene composites filled with calcite (modified with stearic acid) were higher than those of unfilled ones, implying the reinforcing effect of calcium carbonate (Kwon et al., 2002).

CONCLUSIONS

1. Introduction of chalks modified with ammonium salts to HDPE causes a greater increase in MFI than the addition of unmodified chalks. The greatest increase in MFI has been noted for the samples containing chalks in concentrations between 0.05 and 2.0% wt. The presence of chalk modified with the salt containing a greater aliphatic substituent causes a greater decrease in MFI than the presence of chalk modified with the salt containing a smaller substituent.
2. The presence of chalk in HDPE does not affect the course of the polymer crystallisation taking place on foil production. After etching, the SEM of the surface of the foil containing chalk shows the crystalline aggregations identical to those in PE foil without chalk.

3. The addition of chalks modified with ammonium salts causes greater changes in the elasticity modulus than the addition of unmodified chalk. The Young modulus of the former samples is greater. The greatest changes in the Young modulus are observed for PE with chalk modified with the salt containing a greater aliphatic substituent.
4. If the addition of modified chalk changes some properties of HDPE, these changes are always more pronounced for the samples containing chalk modified with the salt with a greater aliphatic substituent.

ACKNOWLEDGEMENTS

This work was supported by a Scientific Grant 2P03B 09919 from the Polish Committee for Scientific Research.

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Domka L., Wąsicki A., Kozak M., *Mikrostruktura i własności mechaniczne nowych kompozytów HDPE-kreda*, Physicochemical Problems of Mineral Processing, 37 (2003) 141-147 (w jęz. ang.).

Nowoczesne przetwórstwo polimerów stawia coraz wyższe wymagania napełniaczom mineralnym stosowanym w kompozytach. Powinny one poza obniżeniem kosztów produkcji kompozytów polimerowych także poprawiać ich własności mechaniczne czy nadawać im nowe jak termostabilność. W pracy przedstawiono metodę otrzymywania kompozytów polietylenu z kredą modyfikowaną dwoma nowymi chlorkami 1-alkoksymetylo-3-hydroksypyrydyniowymi: 3-hydroksy-1-oktyloksymetylopirydyniowym i 3-hydroksy-1-oktadecyloksymetylopirydyniowym oraz scharakteryzowano mikrostrukturę oraz wybrane własności mechaniczne uzyskanych kompozytów. Wprowadzenie do HDPE kred modyfikowanych solami amoniowymi spowodowało większy wzrost MFI stopów niż dodatek kredy nie modyfikowanej. Zmiany MFI widoczne są najwyraźniej dla kompozytów PE zawierających pomiędzy 0,05 i 2,0% wag napełniacza. Dodatek kred modyfikowanych solami amoniowymi powoduje większe zmiany niektórych właściwości wytrzymałościowych (np. moduł sprężystości wzdłużnej) niż kreda nie modyfikowana. Natomiast naprężenie przy zerwaniu mało różniło się w próbkach napełnianych modyfikowanymi i niemodyfikowanymi kredami.