Effect of non-ionic surfactants on the exfoliation and properties of polyethylene-layered silicate nanocomposites

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Abstract

Nanocomposites of high-density-polyethylene (HDPE) and organically (dimethyldioctadecylammonium) modified montmorillonite (OM) were prepared and the effect of non-ionic surfactants on the OM exfoliation and composite properties (tensile + gas-permeation) was studied. Amphiphilic block and random copolymers of different chemical structures were used as dispersing agents. The presence of copolymers in the composites led to polymer intercalation that increased the *d*-spacing and facilitated the exfoliation. Consequently, the permeability coefficient (oxygen) of the nanocomposites was decreased and their stiffness increased. End-functionalized oligomers proved to be more efficient in dispersing the OM than copolymers in which the polar units are randomly distributed along the polymer chain. Poly(ethylene-*co*-vinyl alcohol) increased the *d*-spacing but did not improve the properties of the composite probably due to 'bridging' the silicate layers, which hindered the exfoliation. The OM exfoliation could be enhanced to such an extent that an inclusions' average aspect ratio of 150 was estimated from the oxygen-permeation measurements. With increasing exfoliation, the stiffness, strength and gas-barrier properties of the composites improved significantly. The oxygen permeability of the HDPE nanocomposites was cut to less than half, thus offering a strong barrier to oxygen and humidity useful for food and drug packaging.
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1. Introduction

To meet the rising demands of modern applications, hybrids of inorganic and polymeric materials are continuously developed [1]. Polymer-layered silicate nanocomposites, in which the inorganic phase has a dimension in the range 1–100 nm, have attracted much attention because of the anticipated properties enhancement [2]. A key parameter to nanocomposite performance is optimal dispersion (exfoliation) of their primary 1 nm silicate layers in the polymer matrix because of their high aspect ratio. High degree of exfoliation and consequently impressive properties enhancement have been achieved in polar polymers, such as polyamides, polyurethanes, epoxy resins, etc. by organically modifying the silicate surface [2–6].

Because of its attractive properties, polyethylene (PE) is the world's largest volume thermoplastic and finds wide use in packaging, consumer goods, pipes, cable insulation, etc. Successful development of PE-layered silicate nanocomposites, especially high density PE (HDPE), promises improvements in permeability-barrier and mechanical properties that would open doors for new applications. However, the dispersion of the hydrophilic silicates in a hydrophobic matrix like PE is a real challenge [7,8]. Complete miscibility between the two heterogeneous phases could not be achieved by exchanging the inorganic cations of the aluminosilicates with alkylammonium ions. For the preparation of PE–OM nanocomposites, two approaches have been applied; in situ intercalative polymerization and melt-compounding [7–14]. Although the first offers more homogeneous composites with a better dispersion of the silicate layers, the second is usually preferred because the in situ polymerization leads to polymers of low molecular weight. The dispersion attained by the in situ polymerization method is also thermodynamically unstable. Theoretical studies showed that an interplay of entropic and energetic factors governs the exfoliation process, and that the miscibility between the two phases is a function of the

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Flory–Huggins interaction parameter ($\chi = 0$ is required) [15–17]. For alkyl OMs–PE composites, it has been predicted that only an intercalated structure is possible even if $\chi < 0$. The exfoliation of the OM and the stability of the dispersion were also correlated to the solubility parameters of the two phases [18]. To promote the dispersion of clays in polyolefins, the addition of end-functionalized polymer chains in small quantities has been proposed [19,20]. The functional group is expected to anchor to the clay surface and the polymer chain provides a favourable enthalpy and entropy of mixing with the polymer matrix. Simulation studies also showed that increased polymer-filler attractive interactions (functionalized polymer matrix) may create bridges between adjacent silicate layers, leading to poor intercalation [21].

The use of functionalized polypropylene (PP), maleic anhydride-grafted PP oligomers (PP-*g*-MA), as an additive (compatibilizer) to prepare PP–OM nanocomposites has been early described by Kawasumi et al. [22,23] and studied in detail by Reichert et al. [24]. The silicate exfoliation and properties of the composites were correlated to the MA graft density and weight fraction of the 'compatibilizer'. The different synthetic routes for the preparation of PP–montmorillonite nanocomposites have been reviewed by Manias et al. [25]. In these composites, the elastic modulus and the yield stress were appreciably enhanced, although PP-*g*-MA oligomers were used in high concentrations (20 wt%). Ammonium-terminated PP has been synthesized and used to surface modify montmorillonite, leading to an exfoliated structure but the properties of the composites were not described [26]. Similarly, maleic anhydride-grafted PE (PE-*g*-MA) has been used to prepare PE–OM nanocomposites but much less studies (composites in which PE-*g*-MA was used as a matrix are not considered here) were devoted to PE than to PP [12–14]. PE-*g*-MA was added in concentrations up to 30 wt% and the same conclusions were drawn as for PP, that is, the filler dispersion improved with increasing MA graft density and with increasing weight fraction of PE-*g*-MA. Hotta and Paul [14] studied the influence of PE-*g*-MA addition on the mechanical and permeation properties of linear low density PE composites with octadecyl- and dioctadecyl-OMs. The exfoliation, tensile modulus and yield strength were enhanced with increasing ratio of 'compatiblizer' to OM. The dioctadecyl-OM composites showed better dispersion and mechanical properties than those of the octadecyl-OM. The gas permeability was also decreased by ca. 40% in the dioctadecyl-OM nanocomposites at 0.069 inorganic weight fraction and 13 wt% PE-*g*-MA.

The objective of the present investigation is to study the influence of non-ionic surfactants with different composition and constitution (random and block PE-copolymers) on the OM dispersion as well as on the tensile and gas permeation properties of OM–HDPE nanocomposites. For this purpose, the clay surface was organophilized by fully exchanging its inorganic cations with dimethyldioctadecylammonium ions, avoiding the presence of excess ammonium salt. A correlation between the properties of the nanocomposites, as a measure for the degree of exfoliation, and the dispersant concentration is aspired. HDPE was chosen as a polymer matrix for its importance in food and drug packaging.

2. Experimental part

2.1. Materials

A purified clay, Cloisite Na, was purchased from Southern Clay Inc. (Gonzales, TX, USA). Its cation exchange capacity was determined by exchanging the inorganic cations with $Cu(trien)^{2+}$ to be 0.88 mequiv/g [27,28]. Dimethyldioctadecylammonium bromide (2C18) was procured from Acros Organics (New Jersey, USA). The block-copolymer, polyethylene-*block*-poly(ethylene glycol) (PE-*b*-PEG), and the random-copolymer, poly(ethylene-*co*-vinyl alcohol) (PE-*r*-VOH), were purchased from Aldrich (Buchs, Switzerland). The random-copolymer, poly(ethylene-*co*-methacrylic acid) (PE-*r*-MAA), was obtained from DUPONT (Wilmington, DE, USA) under the trade name 'Nucrel 699', whereas the maleic anhydride grafted PE, poly(ethylene-*graft*-maleic anhydride) (PE-*g*-MA), was obtained from Eastman Chemical Co. (Kingsport, TN, USA) under the trade name 'Epolene C-18'. The polyethylene used is a linear high density PE (Hostalen GF 9055F) that was supplied by Basell (Mainz, Germany). It has a density of 0.954 g/cm^3 (23 °C) and a melt flow index of 0.5 g/10 min (2.16 kg at 190 °C).

2.2. Filler surface treatment

A 8 g sample of the clay was stirred in 400 ml hot (60 °C) deionized water for 1 h and 200 ml ethanol was added. The mixture was sonicated (ultrasonic horn at 60% amplitude) for 10 min, and shear mixed (Ultra-Turrax T25-IKA) for another 10 min. To this dispersion, 7.04 mmol of dimethyldioctadecylammonium bromide dissolved in 200 ml ethanol was added drop wise under stirring and the reaction mixture stirred at 60 °C for 24 h. At the end of the reaction time, the suspension was filtered and the OM thoroughly washed with a hot ethanol–water mixture (1:1) followed by hot ethanol. The product was dispersed (sonicated) and stirred in hot ethylacetate–ethanol (9:1) for 4 h, filtered and dried at 70 °C under reduced pressure. The degree of exchange and the purity of the organic monolayer were monitored by Hi-Res TGA [27,28]. The last step was repeated if the TGA showed the presence of unreacted ammonium salt or local bilayer. The OM was dispersed (sonication) in dioxane (2%), freeze-dried and sieved (60 µm) to obtain a finely divided powder. The OM (density = 1.51 g/cm^3) was free of excess ammonium salt that is usually present in commercial OMs, which impair the thermal stability and other properties of the composites [27–29].

2.3. Composite and test specimen preparation

Since the crystalline inorganic part of the OM is that which enhances the composite properties, the volume fraction of the inclusions should not include that of the organic coating. The required amounts of OM and polymer were calculated on the basis of the desired inorganic volume fraction (0.028) as previously described [7]. The HDPE and OM were compounded in a twin-blade kneader 'Plasti-Corder W 50 EH' (Brabender, Duisburg, Germany) equipped with a 60 cm^3 bowl and counter-rotating blades. The total amount of material was chosen to completely fill the bowl at the compounding temperature, in order to avoid incorporation of air in the composite that promotes polymer degradation. The polymer and amphiphilic copolymer pellets were molten at 160 °C, then the OM was gradually added and the mixture kneaded applying a torque of 20–23 Nm. The duration of this process was 20 min. The amount of the copolymer is given in weight percent of the composite. In case of PE-r-VOH, the compounding temperature was raised to 170 °C. The resulting compounds were compression molded to 1.5 mm thick plaques in a brass frame between two aluminum plates at 180 °C and left to cool slowly in the press without active cooling to ensure reproducible crystallization. The compression molding process was carried out under reduced gas pressure (0.01 mbar) in a brass chamber and the compound was carefully degassed before and during molding to avoid the presence of micro voids. The composite density at room temperature is 0.994 g/cm^3. Pieces of the plaques were pressed in the same way to ca. 60 μm thick films between PET foils using metal spacers to define the film thickness. The exact thickness was calculated from the weight of a film of defined area and its density. Dumbbell-shaped tensile bars were stamped out of the plaques, using a cutting press (H.W. Wallace, Croydon, Surrey, England) with a die conforming to type 5B of the ISO 527-2 norm. For comparison, neat HDPE was processed and tested in the same way as the composites.

2.4. Oxygen permeation

The oxygen transmission rate through films of the nanocomposites and the processed neat polymer was measured using an OX-TRAN 2/20 ML (Mocon, Minneapolis, USA) at 23 °C and 0% RH (relative humidity). The transmission rate was normalized with respect to the film thickness. The density of the polymer and its composites was determined by weighing samples in air and in ethanol using an analytical balance and a home made device similar to the Mettler density-kit ME-33360 (Mettler-Toledo, Greifensee, Switzerland), following the equation:

$$\rho = \frac{\rho_{Et} M}{M - M_\ell}$$

where ρ is the sample density, ρ_{Et} is the density of ethanol at 23 °C, M is the sample mass in air and M_ℓ is its mass in ethanol. The average of four measurements for each sample is reported.

2.5. Tensile testing

Engineering stress–strain curves were obtained from uniaxial tension tests (ISO 527-1) on dumbbell-shaped tensile bars of type 5B (ISO 527-2). The measurements were carried out at room temperature on a Zwick Z020 tensile tester with testXpert 9.01 software (Zwick, Ulm, Germany). The displacement was measured with a Video-Extensometer V4.19.02 (Messphysik, Fürstenfeld, Austria). The elastic modulus was determined at 0.1 mm/min crosshead speed (0.05–0.25% strain), while all other tensile characteristics were measured at 6 mm/min. An average of at least five measurements for each sample is reported.

The transmission electron microscopy (TEM) and wide angle X-ray diffraction (WAX) measurements have been previously described [7].

3. Results and discussion

To study the influence of non-ionic surfactants on the silicate exfoliation and the properties of OM–HDPE nanocomposites, a number of amphiphilic PE-copolymers were chosen on the basis of their chemical and sequential structure. The number of polar units as well as their position in the polymer chain (block or random) was varied. The chemical constitution and number average molecular weight of the copolymers are given in Table 1 in a decreasing order of polarity. PE-g-MA is the additive commonly used in the literature to improve the OM dispersion in PE and is included for comparison. The PE-g-MA used here has low anhydride content so that, on average, there is one anhydride moiety per two molecules. Therefore, it can be considered as an end-functionalized PE oligomer, regardless of the grafting position. PE-b-PEG is a block-copolymer, whose chains contain 33 methylene groups and 2.6 ethylene oxide units per molecule on average; hence it is an end-functionalized PE oligomer with a small polar head group. PE-r-VOH and PE-r-MAA are random copolymers, in which the molecules carry several

Table 1
Molecular weight (number average) and composition of the surfactants[a]

Copolymer	Mn (g/mol)	Weight fraction of polar comonomer	Molar fraction of polar comonomer
PE-r-VOH	Not available	0.69	
PE-b-PEG	575	0.20	0.137
PE-r-MAA	68,000	0.11	0.039
PE-g-MA	5700	0.01	0.003

[a] Supplier data.

polar groups that are randomly distributed along the polymer chain and were chosen because of their ability to form hydrogen bonds with aluminosilicates. The hydroxyl groups of PE-*r*-VOH are of basic nature, while those of PE-*r*-MAA have an acidic character. The concentration of the dispersing agents in the composites was kept low (1.7 wt%), in order not to impair the crystallization and mechanical properties of the polymer matrix. On the basis of the OM and surfactant concentrations in the composites, a copolymer/OM weight ratio of 0.17 can be calculated. Cloisite was chosen on the basis of its relatively high charge density that leads to denser organic coating on exchanging its inorganic cations by alkylammonium ions. It was surface treated with 2C18 because this leads to an OM with an appreciable *d*-spacing (2.51 nm) and low surface energy [7]. Care was taken to fully exchange the inorganic cations, in order to achieve the maximum possible surface coverage, while avoiding the presence of excess ammonium salt in the interlayer [27,28].

The *d*-spacing and oxygen permeability coefficient of the 2.8 vol% composites that contain different amphiphilic copolymers (1.7 wt%) are compared to those of the composite without additives in Table 2. The WAX-diffractograms of the composites with and without surfactants are compared to that of the OM powder in Fig. 1. The fact that in all diffractograms the (001) reflection can be seen indicates that tactoids are present and complete exfoliation was not achieved. It can also be seen that without dispersant the *d*-spacing of the composite is the same as that of the OM powder, indicating that PE was not intercalated. The addition of surfactants increased the *d*-spacing to different extents, depending on the number of polar units in the copolymer molecule except for PE-*g*-MA. That is, the copolymer was more intercalated with increasing polarity of the molecule. PE-*g*-MA had no influence on the *d*-spacing as can also be seen in the diffractograms shown in Refs. [13, 14]. The broad peak observed in the diffractograms (Fig. 1) of the OM and its PE composites at ca. 7.1° 2Θ ($d=$ 1.25 nm) can be the (002) of the OM or the (001) of sodium montmorillonite. However, the (001) reflection of pristine montmorillonite is usually much sharper and the TGA analysis showed that the inorganic ions were fully exchanged. Therefore, this peak can be safely assigned to the higher order reflection of the OM. The (001) peak width

Table 2
Effect of copolymers on the *d*-spacing and oxygen permeability of 2.8 vol% composites (copolymer/OM weight ratio=0.17)

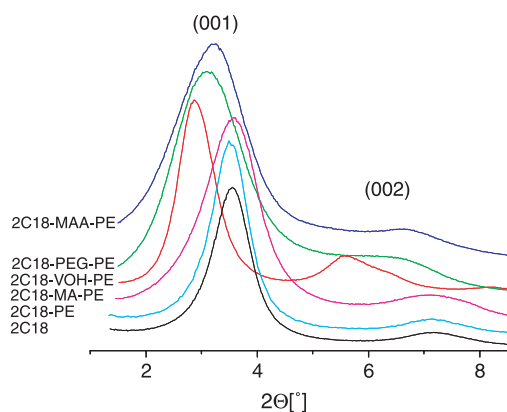| Copolymer (1.7 wt%)	d_{001} (nm)	Permeability coefficient (cm^3 μm/m^2 day mmHg)
Neat HDPE		54
No copolymer	2.51	37
PE-*r*-VOH	3.05	36
PE-*b*-PEG	2.86	31
PE-*r*-MAA	2.71	32
PE-*g*-MA	2.43	33

Fig. 1. WAX patterns of the OM (2C18) powder and its HDPE composites (0.028 inorganic volume fraction) with and without surfactants.

of the composite containing PE-*r*-VOH is smaller than that of all other composites, indicating that the tactoids thickness or the coherence length of the crystalline domains in this composite is larger than in the others. Since the intensity of the reflections depends on the orientation of the tactoids as well as on their concentration, it cannot be used to estimate the concentration of the tactoids.

Although the polymer was not intercalated in the OM–HDPE composite (without dispersant), the permeability coefficient was decreased due to partial exfoliation of the OM [7,30]. The addition of amphiphilic copolymers increased the *d*-spacing and decreased the permeation coefficient further, indicating better exfoliation (Table 2). However, the most polar surfactant, PE-*r*-VOH, that was more intercalated than the others did not lead to a decrease in the permeability coefficient, suggesting that the exfoliation was hindered. This may be due to strong hydrogen bonds between different silicate layers and the same copolymer chain, hence 'bridging' the layers and hindering their exfoliation. This 'bridging' effect led to larger coherence length and sharper (001) reflection of the crystalline domains (Fig. 1). No 'bridging' between the silicate layers took place in presence of PE-*r*-MAA, probably due to the low molar fraction of the polar units in this copolymer or to the acidic nature of its OH groups (Table 1). Although PE-*g*-MA did not increase the basal-plane spacing, it was as efficient as PE-*b*-PEG and PE-*r*-MAA in decreasing the permeation coefficient. This indicates that exfoliation took place, i.e. most of the tactoids that were intercalated by PE-*g*-MA were exfoliated. These results confirm that the exfoliated OM layers are those, which contribute to the properties enhancement in nanocomposites and not the intercalated tactoids as was previously shown in OM-epoxy composites [31]. This can be rationalized by recalling the dependence of composite properties (mechanical and permeation) on the aspect ratio of the inclusions [32–37]. The polymer intercalation leads to an increase in *d*-spacing, which reduces the attraction between the silicate layers and facilitates the exfoliation during shearing but the exfoliated layers are those which

enhance the nanocomposite properties. The remaining unexfoliated but intercalated tactoids have low aspect ratio and do not contribute much to the composite properties enhancement. At this point, we would like to note that the surfactants concentration was kept low (1.7 wt%) and the presence of the OM showed no influence on the crystallinity of HDPE under the processing conditions (slow cooling) used [7,8,30]. Therefore, the observed changes in permeability are mainly due to differences in the degree of exfoliation. Fig. 2 shows the exfoliated layers and very thin tactoids present in the OM–(PE-*b*-PEG)–HDPE nanocomposite, confirming the presence of mixed morphology (extending from single layers to pristine OM tactoids). It can also be seen in Fig. 2 that these inclusions are misaligned, which strongly influences the barrier performance of the composites [34–37]. However, observing the same specimen at different magnifications (Fig. 3) shows that the platelet orientation is length-scale dependent. Unfortunately, at low magnifications, where a distinct orientation can be observed, only the tactoids are seen and the exfoliated 1 nm thick layers cannot be detected. At the moment, it is not clear, whether the exfoliated layers and the

tactoids are differently oriented (the tactoids may be easier to orient in the shear flow because they are stiffer) or the inclusions' orientation is not perfect, making it observation-scale dependent. The same observation was made in the composite without dispersing agents [7].

The tensile properties of the OM–HDPE nanocomposites with and without amphiphilic copolymers are compared to those of the neat polymer in Table 3. Without surfactant, the elastic modulus of the nanocomposite was 25% higher than that of the neat HDPE due to partial exfoliation of the OM, while the yield stress remained unaffected. On the other hand, the yield strain and stress at break were reduced. The addition of surfactants reduced the modulus of the composites back to that of the neat polymer, although they were added in very small quantities (1.7 wt%), except in case of PE-*b*-PEG, where the modulus was slightly enhanced. The decrease in modulus on adding copolymers is probably due to the often observed plasticizing effect of amphiphilic molecules. Fig. 4 shows a slight increase in the relative modulus with increasing *d*-spacing (resulting from the copolymer addition), which is the sum of both effects; exfoliation and plasticization. PE-*b*-PEG enhanced the relative modulus more than the other surfactants, which may be due to its chemical structure (end-functionalized). However, it is difficult to determine whether the polar head group anchors to the silicate surface as proposed by Balazs et al. [19,20] or the amphiphilic molecules simply reduce the interfacial tension between the PE and the OM. The presence of PE-*r*-VOH in the composite reduced the yield stress and stress at break but had little influence on the yield strain due to its strong intercalation and to bridging the silicate layers (Table 3). The other copolymers decreased the yield stress of the composite only slightly and increased the yield strain due to their plasticizing effect. Fig. 4 shows that the decrease in relative yield stress and strain correlate to the increase in *d*-spacing, while the relative stress at break is independent of this parameter but at a low level (ca. 0.5). This supports the assertion often made that tactoids in nanocomposites with mixed morphology are responsible for
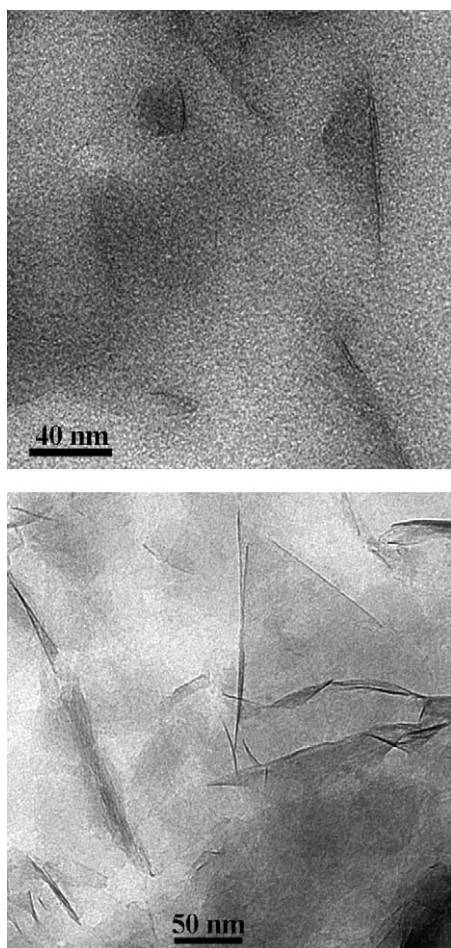

Fig. 2. TEM micrographs of the OM–(PE-*b*-PEG)–HDPE nanocomposite (3.4 wt% PE-*b*-PEG). The dark lines are cross-sections of aluminosilicate layers.

Table 3
Effect of copolymers on the tensile properties of 2.8 vol% composites (copolymer/OM weight ratio=0.17)

Copolymer (1.7 wt%)	Elastic modulus[a] (MPa)	Yield stress[b] (MPa)	Yield strain[c] (%)	Stress at break[d] (MPa)
Neat HDPE	1020	26	9.6	36
No copolymer	1270	26	7.6	21
PE-*r*-VOH	1080	23	7.9	15
PE-*b*-PEG	1320	25	8.1	17
PE-*r*-MAA	1080	25	8.4	14
PE-*g*-MA	1030	25	8.9	15

[a] Relative probable error 5%.
[b] Relative probable error 2%.
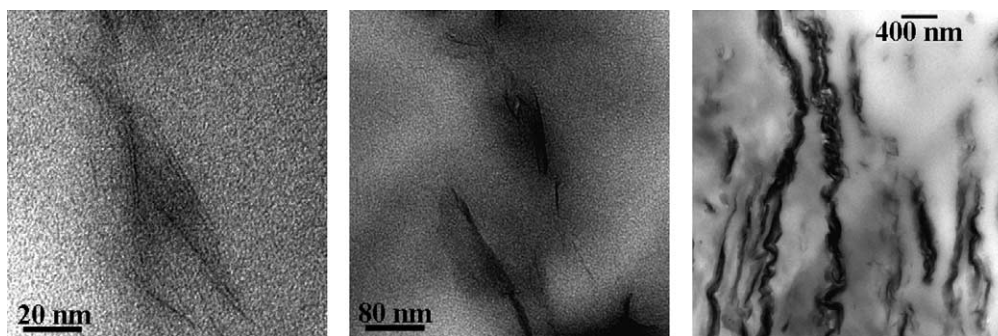[c] Relative probable error 4%.
[d] Relative probable error 10%.

Fig. 3. TEM micrographs of the OM–(PE-*b*-PEG)–HDPE nanocomposite (3.4 wt% PE-*b*-PEG) at different magnifications showing the length scale dependence of the inclusions' orientation. The dark lines are cross-sections of aluminosilicate layers.
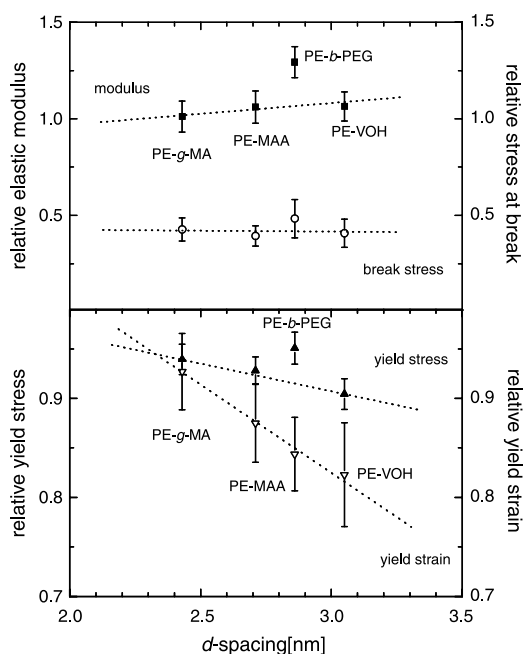

Fig. 4. The relative tensile properties of the OM–copolymer–HDPE nanocomposites plotted as a function of their *d*-spacing. The dotted lines are simply guide lines for the eye.
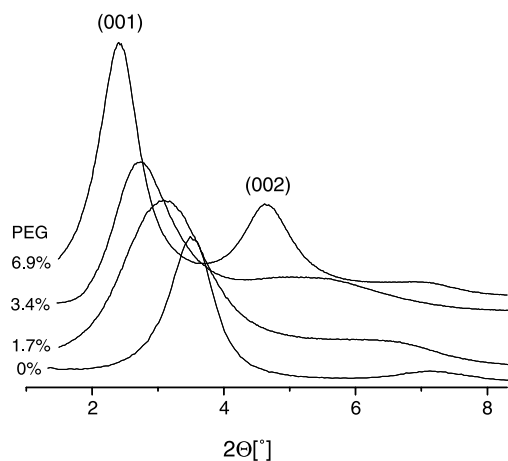
the deterioration of tensile properties. Tactoids with larger *d*-spacing are expected to be easier to disintegrate under stress, leading to premature failure during tensile testing.

To study the effect of increasing the dispersant concentration on the silicate exfoliation and properties of the nanocomposites, PE-*b*-PEG was chosen because of its favourable influence on both tensile and gas-barrier properties. The development of the WAX reflections with increasing copolymer concentration in 2.8 vol% composites is shown in Fig. 5. As can be seen, the (001) basal-plane reflection shifts to lower angles with increasing surfactant concentration, indicating more polymer intercalation. Up to 7 wt%, the (001) could be detected, indicating that complete exfoliation was not achieved and that OM tactoids are still present. The (001) peak-width initially increased upon intercalating the copolymer due to inhomogeneous intercalation but decreased as the copolymer concentration increased, indicating better homogeneity of the *d*-spacing. The basal-plane spacing is also plotted as a function of the PE-*b*-PEG concentration in Fig. 6, showing a linear dependence and suggesting that increasing the copolymer concentration further will probably lead to larger *d*-spacing. The oxygen permeability coefficient of the composites with increasing copolymer concentration is compared to those of the composite without dispersant; neat HDPE and HDPE-copolymer blend in Table 4. As can be seen, the copolymer (3.4 wt%) did not influence the oxygen permeability
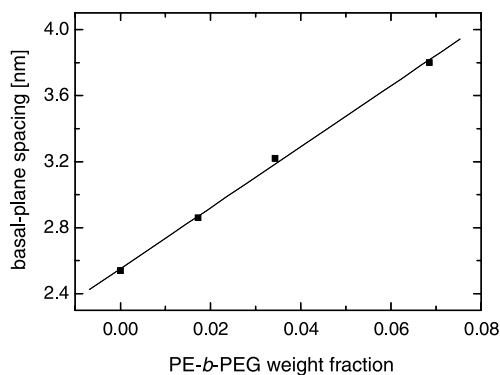

Fig. 5. WAX patterns of the OM–(PE-*b*-PEG)–HDPE nanocomposites with different copolymer concentrations.

Fig. 6. Influence of the PE-*b*-PEG concentration on the *d*-spacing of the composites.

Table 4
Effect of PE-*b*-PEG weight fraction on the *d*-spacing and oxygen permeability of 2.8 vol% composites

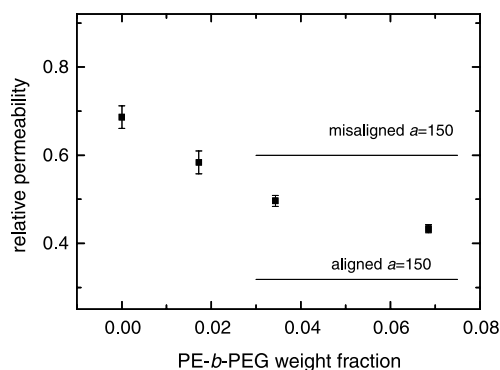| PE-*b*-PEG (wt%)	Copolymer/ OM wt. ratio	d_{001} (nm)	Permeability coefficient (cm^3 $\mu m/m^2$ day mmHg)
Neat HDPE			54
3.4 No filler			53
0.0	0.00	2.51	37
1.7	0.17	2.86	31
3.4	0.33	3.12	27
6.9	0.67	3.63	24

Fig. 7. Effect of the PE-*b*-PEG concentration on the relative oxygen permeability of the composites.

through HDPE, indicating that it has no effect on its crystallinity or crystallite size under the processing conditions used. In contrast, the permeability coefficient of the composites steadily decreased with increasing PE-*b*-PEG concentration, indicating progressive exfoliation. Unfortunately, no quantitative information on the exfoliation progress could be obtained from the TEM micrographs because of difficulties in achieving thin sections of high quality that are necessary to get statistically relevant data. The relative permeability (composite/HDPE) is plotted as a function of the surfactant weight fraction in Fig. 7, showing an asymptotic decrease with increasing copolymer concen-

tration. The numerically calculated values for parallel oriented and randomly disordered round platelets with an aspect ratio of 150 are also indicated in Fig. 7 as solid lines [35–37]. Since the measured permeation coefficient lies between the two lines and recalling that the inclusions in the prepared nanocomposites are partially aligned, it is reasonable to assume that they have an average aspect ratio of ca. 150 in the composite with 6.9 wt% copolymer. An average aspect ratio between 50 and 150 was estimated for the inclusions in the OM–HDPE composite without surfactant [7]. At 6.9 wt% PE-*b*-PEG, the oxygen permeability coefficient of the nanocomposite was reduced by 55%, hence offering an outstanding barrier for both oxygen and humidity.

The tensile properties of the nanocomposites were also measured as a function of increasing PE-*b*-PEG weight fraction and are compared to those of the composite without dispersant, neat HDPE and a blend of HDPE with the copolymer in Table 5. As can be seen, the copolymer had little effect on the tensile properties of HDPE in line with the permeability results, so that significant changes in the composite properties on adding the surfactant can be safely attributed to OM exfoliation. The relative values (composite/HDPE) are also plotted as a function of the copolymer concentration in Fig. 8. Obviously, the elastic modulus increased linearly with increasing exfoliation, in line with theoretical calculations recently presented by Sheng et al. [38]. Both yield stress and stress at break steadily increased with augmenting copolymer concentration (increased exfoliation) after an initial small drop, resulting from the surfactant plasticizing effect. The copolymer had the same effect on the yield strain with an opposite sign, indicating that the composites became less ductile. However, the loss in ductility is quite modest compared to the gain in the other tensile properties. It is to be noted that the stress at break and the yield stress decreased with increasing inorganic volume fraction in composites without surfactant [8]. This confirms that the presence of appreciable amounts of tactoids lead to premature failure, while the exfoliated layers strengthen the material.

Table 5
Tensile properties of HDPE and its 2.8 vol% nanocomposites as a function of PE-*b*-PEG weight fraction

PE-*b*-PEG (wt%)	Copolymer/OM wt. ratio	Elastic modulus[a] (MPa)	Yield stress[b] (MPa)	Yield strain[c] (%)	Stress at break[d] (MPa)
Neat HDPE		1020	26	9.6	36
3.4 No filler		1060	26	11.4	35
0.0	0.00	1270	26	7.6	21
1.7	0.17	1320	25	8.1	17
3.4	0.33	1450	28	7.2	19
6.9	0.67	1620	29	6.9	28

[a] Relative probable error 5%.
[b] Relative probable error 2%.
[c] Relative probable error 4%.
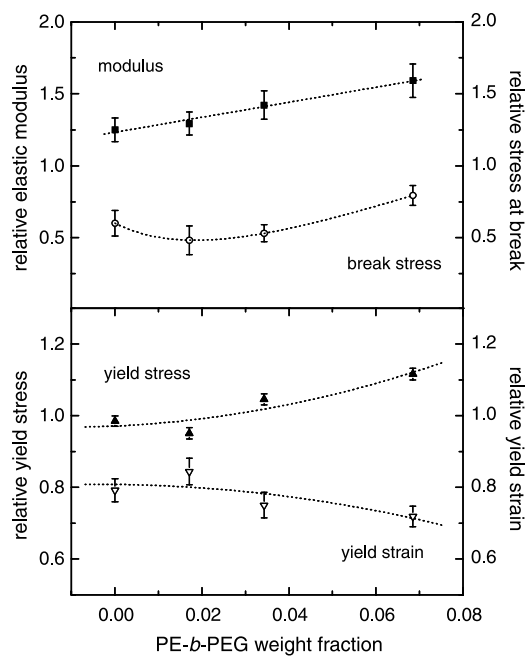[d] Relative probable error 10%.

Fig. 8. The relative tensile properties of the OM–(PE-*b*-PEG)–HDPE nanocomposites as a function of the copolymer concentration. The dotted lines are simply guide lines for the eye.

4. Conclusions

Non-ionic dispersing agents help to exfoliate alkylammonium-modified montmorillonite in polyethylene, thus enhancing the tensile and gas-barrier properties of the polymer. Amphiphilic copolymers intercalate the OM tactoids, hence increase the *d*-spacing and decrease the attraction between the silicate layers. This facilitates the exfoliation of the highly anisometric layers, which enhance the properties of the composites. The intercalated tactoids themselves do not contribute much to the composite performance. With increasing exfoliation, the stiffness, strength and gas-barrier properties of the composites significantly improve. The effect of the copolymers increases with increasing concentration and polarity. End-functionalized molecules are more efficient than random copolymers, which may bridge the silicate layers and hinder the exfoliation. The montmorillonite platelets are not perfectly aligned and their orientation is a function of the observation scale.

Acknowledgements

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