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Lime Repellent Polyethylene Additives

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ABSTRACT: The precipitation of calcium carbonate from hard water, commonly known as calcification or scaling, is a widespread nuisance. To avoid scaling, a physical or chemical pretreatment of water is often employed, such as ion exchange, addition of complexing agents, or the use of magnetic and electric fields. Our approach is to construct surfaces to which calcium carbonate crystals do not adhere. Here, we show that by the use of particular copolymer additives, polyethylene can be made lime repellent. The copolymers have the formula: polyethylene-*block*-poly(ethylene glycol) and are compounded into the polyethylene. Twelve such additives were investigated and three displayed anticalcification activity. The effective copolymers were investigated by mass spectrometry. Infrared spectroscopy of copolymer/polyethylene blends revealed that the concentration of the additive in the matrix correlates to a specific absorption band. Stability tests against hot water showed that the anticalcification activity was maintained over the timeframe investigated. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 2727–2734, 2013

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INTRODUCTION

Additives are essential for the processing and use of plastics, serving to fine-tune material properties for the desired application. The admixing of substances into the plastic melt is called compounding and through compounding an improvement of the chemical, electrical, and mechanical properties can be achieved. There are many categories of additives, such as antioxidants, light stabilizers, acid scavengers, lubricants, polymer-processing aids, antiblocking additives, slip agents, antifogging additives, antimicrobials, flame retardants, chemical blowing agents, and colorants.[1]

Here, we report on a new application of additives. We describe additives which render polyethylene (PE) lime repellent, that is, which impede the adhesion of calcium carbonate crystals to the PE surface. In many applications, calcification, or scaling, is an issue. Sanitary installation is an example where calcification can lead to malfunction or even complete failure of the equipment, resulting in costly cleaning, replacement, or repair. Therefore, surfaces which prevent calcium carbonate deposition from aqueous solution are of great interest. In a previous article,[2] we presented lime repellent sol–gel coatings for glass and some plastics. As an alternative, here we investigate the application of additives,[3] which are easy to use: it is sufficient to simply add them to the polymer melt. The requirements for a successful anticalcification additive are effectiveness against the adherence of calcium carbonate, longevity, stability, and low cost.

The state-of-art methods in resisting lime rely on a pretreatment of hard water either by chemical or by physical methods.[2] Appropriate chemicals can reduce the concentration of calcium ions by complexation in such a way that the solubility product of calcium carbonate is undershot. Further, scale-forming ions may be removed from hard water by ion exchange. Physical methods are, for example, distillation or the use of electric and magnetic fields.

In a patent, Mayes et al.[4] described the use of comb polymers comprising PEG side chains as antifouling additives for the preparation of, for example, polymeric membranes. The segregation of the comb polymer to the surface is disclosed and antifouling properties of the composite are depicted. However, the matrix polymer in their study is polymethyl methacrylate and antifouling stands for the prevention of adsorption of biomolecules, namely proteins. Neither PE as the target plastic nor lime as the contaminant is mentioned. To the best of our knowledge, there is no comparable approach besides ours that avoids deposition of lime to PE surfaces using polyethylene-*block*-poly(ethylene glycol) (PE-*b*-PEG) copolymers.

As lime repellence is desired on the surface of the material, the additive has to migrate to the surface during, or shortly after,

processing. Migration to the surface is well known for a number of additives, most prominently for slip agents,[5] which provide surface lubrication during and immediately following the processing of polyolefins. Compounded into the plastic, the additive acts as an internal lubricant that gradually migrates to the surface. For this purpose, oleamide and erucamide, which are the amides of the fatty acids oleic acid and erucic acid, respectively, are commonly employed.[1] Both are monounsaturated acids whereby erucic acid is four CH_2-units longer than oleic acid. Owing to the polar amide functionality, the slip agents are incompatible with the nonpolar PE matrix. During and just after extrusion or injection molding, the additive is uniformly distributed in the polymer. As the polymer cools, the slip additive migrates to the outer surface and forms an incomplete layer. First, a monolayer is formed on the PE surface and with the arrival of more molecules, more layers are subsequently established. For our purpose, the arrangement of the first layer is of most interest[6] as the molecules are not randomly distributed but show an alignment. This alignment is a consequence of the structure of the additive, which consists of a polar amide head group and a nonpolar hydrocarbon tail. Owing to the affinity of the hydrocarbon tail for the PE matrix, it is embedded in the plastic, whereas the amide group is segregated and faces the air. This structural model is important for the later discussion of the effect of our additives.

We note that the hydrocarbon tail of the slip additive oleamide is the same as in two of our three anticalcification additives. Similar considerations concerning the structure of the first layer should therefore apply.

The anticalcification effect is brought about by poly(ethylene glycol) (PEG). As described previously, surface-bound PEG impedes the adhesion of calcium carbonate crystals in aqueous solution.[2,7] This effect might be related to the known property of surface-bound PEG repelling biomolecules.[8]

Using the above considerations, the ideal composition for an anticalcification additive for PE can be derived. On the one hand, it should consist of a nonpolar tail which serves as an anchor and fixes the additive in the matrix. This "anchor" should be chemically similar to the PE matrix; a hydrocarbon chain is therefore preferred. The second part of the additive serves two purposes. First, it must be incompatible with PE so that the additive migrates to the surface. Second, it should bring about the anticalcification effect. Both prerequisites are fulfilled by PEG. The formula of a possible anticalcification additive for PE is therefore polyethylene-*block*-poly(ethylene glycol) or PE-*b*-PEG.

A molecule of the structure PE-*b*-PEG is an example of a diblock copolymer. The segregation of diblock copolymers to surfaces[9] and interfaces[10] in polymers and polymer blends has been studied experimentally[11,12] and theoretically.[13,14]

Compounds with the structure PE-*b*-PEG are commercially available in large varieties and quantities, and serve as nonionic surfactants or emulsifiers. The hydrocarbon part is often a fatty alcohol derived from natural fats and oils. Fatty alcohol derivatives from lauric, palmitic, stearic, or oleic acid are often used. The fatty alcohols are then ethoxylated to give the PE-*b*-PEG. As a consequence of the ethoxylation process, the number of ethylene oxide units is not fixed but shows a distribution (*vide infra*). Nonionic surfactants of the type discussed above are stable against acids and bases and find broad application in personal care, textile processing, crop protection, etc.[15]

Because of the amphoteric character of PE-*b*-PEG, it can form micelles in aqueous solutions, and reversed micelles in nonpolar solutions. Micelles are spherical aggregates of surfactants with the hydrophilic "head" regions in contact with the water and the hydrophobic "tail" regions in the center of the sphere. This type of micelle is known as normal phase micelle. Reversed (also called inverted) micelles have the "head" group at the center with the "tails" extending out; they are found in nonpolar solvents.[16] Micelles are formed if the concentration of the surfactant reaches or surpasses the "critical micelle concentration" (CMC).[17]

The PE-*b*-PEG additives might form reversed micelles in the PE melt, with the PEG groups inside the spheroid and the hydrocarbon chains stretching out. Such a formation of reversed micelles of the additive in the liquid PE is highly undesirable, because then the additive would no longer migrate to the surface, and the amount of material forming the micelle would be lost. A high CMC of the PE-*b*-PEG additive in PE is therefore required. Although normal phase CMCs are known for some PE-*b*-PEG compounds at ambient temperature in water (Table I),[18–20] we did not find reverse CMCs for those additives in the PE melt. Also, the CMC is temperature dependent and should therefore be known at the temperature of the molten PE.

EXPERIMENTAL

The PE used was a high-density Borstar ME3440 type from Borealis, with 2% carbon black as filler material. The additives **1**–**12** were obtained from Sigma-Aldrich, Buchs, Switzerland.[20] One sample of surfactant **6** for the mass spectrometry study was obtained from Croda, Snaith, England.[15] For the production of PE blends, two extruders were employed. At the lab scale, a noncontinuous twin-screw extruder Haake MiniLab Micro Rheology Compounder (Thermo Scientific, Karlsruhe, Germany), with 7 mL volume was used to prepare strands of PE and PE blends. The procedure for the preparation of the samples summarized in Table II is as follows: The mini-extruder was heated to 150°C and then charged with 2.75 g of PE granules; 0.275 g of the respective additive and then 2.75 g of PE were added. The rotational speed of the screws, turning in the same direction, was 50 rpm. After 12 min, the PE blend was extruded to form strands of approximately 5 mm width.

The production of PE plates containing 4% additive **7** was performed as described in the following sections.

Compounding

The PE compound with additive **7** was produced on a Buss compounder, type MDK 46 with 11 D processing zones. Additive **7** (4%) was premixed with the PE granulate in a drum. The additive/granulate mixture was directly fed into the feeding zone of the compounder. The melt temperature was 200°C and the throughput 10 kg/h. The melt passed directly to a strand extruder. The strand passed a cooling line and was cut into pellets in a granulator. The pellets were dried in hot air and stored in PE bags.

Table I. Properties of Additives Investigated

Compound no.	Chemical name[a]	Trade name[b]	Old trade name[b]	Formula[c]	Molecular weight[d]	CMC (mM)
1	POE(4) lauryl ether	Brij L4	Brij 30	$C_{12}E_4$	362	0.004[e]
2	POE(2) cetyl ether	Brij C2	Brij 52	$C_{16}E_2$	330	0.000067[e]
3	POE(10) cetyl ether	Brij C10	Brij 56	$C_{16}E_{10}$	682	0.002[e]
4	POE(10) stearyl ether	Brij S10	Brij 76	$C_{18}E_{10}$	710	0.003[e]
5	POE(100) stearyl ether	Brij S100	Brij 700	$C_{18}E_{100}$	4670	0.020[e]
6	POE(2) oleyl ether	Brij O2	Brij 93	$C^*_{18}E_2$	356	24.845[e]
7	POE(10) oleyl ether	Brij O10	Brij 97	$C^*_{18}E_{10}$	708	0.940[e]
8	POE(20) oleyl ether	Brij O20	Brij 98	$C^*_{18}E_{20}$	1148	0.265[e]
9	POE(12) tridecyl ether	466417[f]		$C_{13}E_{12}$	728	0.2[g]
10	POE(18) tridecyl ether	466875[f]		$C_{13}E_{18}$	992	
11	PE-*b*-PEG	458988[f]		$C_{33}E_{10}$	920	0.03[h]
12	PE-*b*-PEG	458961[f]		$C_{50}E_{16}$	1400	0.04[h]

[a]POE, polyoxyethylene; PE, polyethylene; PEG, poly(ethylene glycol); [b] Brij® is a registered trademark of Croda International PLC.[14]; [c] C, number of carbon atoms in the hydrocarbon chain; *hydrocarbon chain contains a *cis* double bond; E = —OCH_2CH_2—; —OH terminated.; [d] Of main component, corresponding to chemical name; or as given by the supplier.[19]; [e] CMC in water at 298 K.[17]; [f] Ord. no. from Sigma-Aldrich®.[19]; [g] CMC in water at 298 K.[18]; [h] CMC in water at 298 K.[19]

Table II. Calcification of PE strands Containing Additive

Chemical name[a]	Formula[b]	Fraction of additive (%)	$CaCO_3$ relative to reference (%)[c]
POE(4) lauryl ether (**1**)	$C_{12}E_4$	4.8	98 ± 13
POE(2) cetyl ether (**2**)	$C_{16}E_2$	4.8	96 ± 8
POE(10) cetyl ether (**3**)	$C_{16}E_{10}$	4.8	77 ± 4
POE(10) stearyl ether (**4**)	$C_{18}E_{10}$	4.8	48 ± 11
POE(100) stearyl ether (**5**)	$C_{18}E_{100}$	4.8	89 ± 19
POE(2) oleyl ether (**6**)	$C^*_{18}E_2$	4.8	29 ± 8
POE(10) oleyl ether (**7**)	$C^*_{18}E_{10}$	4.8	28 ± 5
POE(20) oleyl ether (**8**)	$C^*_{18}E_{20}$	4.8	69 ± 9
POE(12) tridecyl ether (**9**)	$C_{13}E_{12}$	4.8	87 ± 5
POE(18) tridecyl ether (**10**)	$C_{13}E_{18}$	4.8	66 ± 6
PE-*b*-PEG (**11**)	$C_{33}E_{10}$	4.8	22 ± 6
PE-*b*-PEG (**12**)	$C_{50}E_{16}$	4.8	93 ± 8

[a]POE, polyoxyethylene; PE, polyethylene; PEG, poly(ethylene glycol); [b] C, number of carbon atoms in the hydrocarbon chain; *hydrocarbon chain contains a *cis* double bond; E = —OCH_2CH_2—; —OH terminated; [c] ±Standard deviation.

Injection Molding

Plates (50 × 100 × 2 mm) were produced in an injection molding machine (Engel, type ES 240/75 to CC90) using the following parameters:

Melt temperature: 210°C; mold temperature: 20°C

Hold pressure: 700 bar; back pressure: 6 bar

Smaller samples with dimensions 50 × 30 × 2 mm were punched from the plates and used in the calcification experiments.

The test rig which allows for controlled and reproducible calcium carbonate deposition has been previously described elsewhere.[2] Six liters of a solution which is 10 m*M* in $NaHCO_3$ and 5 m*M* in $CaCl_2$ is employed as source of the $CaCO_3$. This solution is prepared in a storage vessel which is kept at 20°C. The solution is pumped through the test block where nine plates (Figure 1) await calcification. Alternatively, nine strands (100 mm long and 5 mm wide) of blended and unblended PE can be calcified. The samples are submerged in a laminar flow of the solution during exposure. Standard calcification is carried out for 16 h. Thereafter, the samples are dipped in deionized water to remove weakly adhering $CaCO_3$ and dried. The calcified samples are weighed, the calcium carbonate is wiped off, and the samples are weighed again. The amount of adhering $CaCO_3$ is thus determined.

Mass spectra were acquired at the Laboratory for Organic Chemistry, ETH Zürich, Switzerland. Samples were prepared by

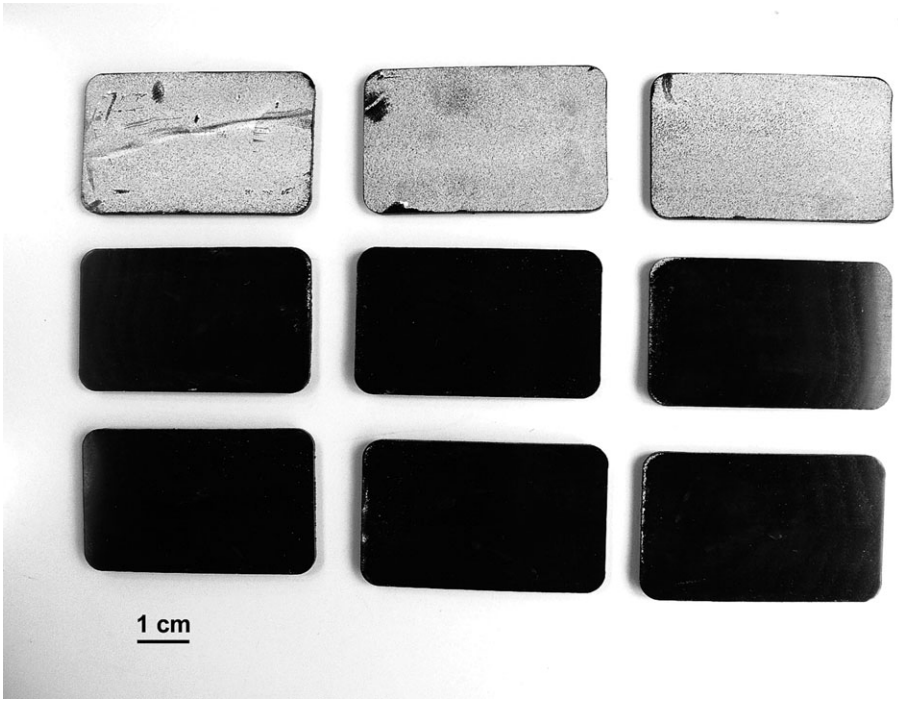

Figure 1. Nine black PE plates after calcification. Top row: Three untreated PE plates, calcified. Middle and bottom rows: Six PE plates containing 4% POE(10) oleyl ether (**7**), lime free.

dissolving 0.1 mg sample (**6**, **7**, or **11**, respectively) in 500 μL methanol. In total, 5 μL was withdrawn and diluted with 950 μL methanol and 50 μL of 1% sodium acetate solution in methanol was added. In brief, 10 μL of the above solution was analyzed using flow injection analysis (Agilent 1200 HPLC-System) on a Bruker maXis (ESI-Q-TOF) using an electrospray ionization source (ESI-source) (Bruker Apollo, Bremen, Germany). Measurement was performed in the positive mode at 200°C and +4 kV. The MS-system was calibrated externally (Agilent Tunning Mix No. G1969-85000) in the enhanced quadratic mode using four measuring points (*m*/*z*: 322, 622, 922, and 1222). Data analysis was performed using Bruker Data-Analysis 4.0 and Polytools 1.12.

The IR spectra were recorded on a Perkin Elmer Spectrum 100 Series and a Bruker Vertex 70 instrument. All samples were wiped three times with an isopropyl alcohol soaked tissue before the measurement. For the correlation study shown in Figure 7, 10 independent spectra from one sample were recorded. The 10 sampling positions were chosen randomly on the strands. Data analysis was performed using the program OPUS.

RESULTS AND DISCUSSION

As discussed in the **INTRODUCTION** section, a candidate anticalcification additive for PE should have the formula PE-*b*-PEG. There are many such compounds on the market and we decided to investigate mainly nonionic surfactants because of their variety. Also, of the nonionic surfactants investigated, an ether group connects PEG with a hydrocarbon chain. The ether link is more stable against hydrolysis than an ester group, as found in ethoxylated fatty acids. Table I summarizes the properties of the additives used in this study.

The hydrocarbon chain should not be too short to obtain a stable anchoring of the additive in the matrix and therefore longer hydrocarbon chains are preferred. However, the migration of the additive to the surface is size dependent and becomes more difficult as molecular weight increases.[21] Therefore, a compromise has to be made. We investigated hydrocarbon chains ranging from 12 to 50 carbon atoms long. As a consequence of their biological origin, some hydrocarbon chains are monounsaturated. This applies especially to the additives stemming from oleic alcohol which contain a double bond in the *cis* configuration at the C9–C10 position (compounds **6**, **7**, **8**, Table I; also compare Figure 3). Additives derived from stearyl alcohol have the same number of carbons as the oleic alcohol derivatives but are saturated (compounds **4** + **5**, Table I). The nonionic surfactants **7** and **4** are therefore differentiated only by the two hydrogen atoms or one double bond found in the hydrocarbon chain, respectively. However, it is seen that the CMC in water at room temperature differs significantly for surfactants **7** and **4** (Table I). The CMC for surfactant **7** is about 300 times larger than for surfactant **4**. Also, the melting points of the two compounds differ: surfactant **7** is semiliquid at room temperature, whereas surfactant **4** is a solid. This demonstrates that a small variation in the molecular formula produces a large difference in some of the physical properties of the two compounds. It is therefore not surprising that surfactants **4** and **7** display different anticalcification behavior.

The additives polyoxyethylene (POE(12)) tridecyl ether (**9**) and POE(18) tridecyl ether (**10**) consist of mixtures of C_{11} to C_{14} *iso*-alkyl ethers with C_{13} *iso*-alkyl predominating.[20]

Few structural details are available concerning the two PE-*b*-PEG additives (compounds **11** and **12**, Table I). Half of their molar mass is PEG, the other half PE,[20] which leads to the formula given in Table I.

The PE-*b*-PEGs (**1**–**12**, Table I) were compounded into the PE in a mini-extruder at a concentration of 4.8%. After extrusion, the strands were calcified as described in the **EXPERIMENTAL** section. Table II summarizes the results, comparing the amount of $CaCO_3$ on the strand containing additive relative to an untreated PE strand. Three strands from the same batch were calcified; the mean and standard deviation of the relative calcification are also listed in Table II. (The lower the percent calcification, the stronger is the effect of the additive). For the additives with <50% calcification (compounds **4**, **6**, **7**, and **11**), the whole process was repeated three times. Hence, three PE samples containing 4.8% of the respective additive were prepared, three strands of which were calcified at one time. We arbitrarily set the limit for good anticalcification efficiency at 30% relative calcification. By doing so, three compounds (**6**, **7**, and **11**) were selected which displayed a good effect against the adherence of lime on PE. As surfactant **7** is cheaper than surfactant **6**[20] and better defined than PE-*b*-PEG **11** (*vide infra*), it was selected as the standard additive.

Figure 1 shows the result from an experiment using a different compounder/extruder, which allowed larger amounts of PE to be processed and plates were produced by injection molding. The commercial PE used in our experiments is dyed black; therefore, the white lime is easily visible. In Figure 1, nine PE samples were calcified together over 3 days. The topmost row consists of three PE samples without additive, whereas the middle and bottom rows are composed of six samples, each containing 4% of surfactant **7**. It is evident that lime is deposited only on the untreated PE, whereas the samples with additive are lime free. (The white stripe to the right of the rightmost plate in the middle row is a light reflection and not calcium carbonate). Therefore, the visual inspection of the plates gives a relative calcification of about 0%. The reason why the PE strands with surfactant **7** were calcified to 28%, but the corresponding injection-molded plates are lime free, is not clear. It might be caused by the different processing of the blends or the possibly higher surface roughness of the strands.

From various other experiments, it was found that the minimal amount of additive **7** leading to an anticalcification effect lies between 2 and 3%.

Owing to the irregular shape of the strands, water contact angles could not be determined. It is, however, possible to measure water contact angles on the plates. PE plates without additive possess a water contact angle of 84 ± 3°, whereas PE plates containing 4% of additive **7** display a water contact angle of 73 ± 3°. Presumably, the PEG chains render the surface more hydrophilic.

To analyze the composition of the three effective additives (**6**, **7**, and **11**) ESI mass spectrometry was chosen (ESI-Q-TOF). Figure 2 shows a deconvoluted, high-resolution mass spectrum of commercially available surfactant **7** (Figure 3). The high resolution of the spectrum allows the assignment of molecular formula to the respective peaks. Sodium adducts of fatty alcohol

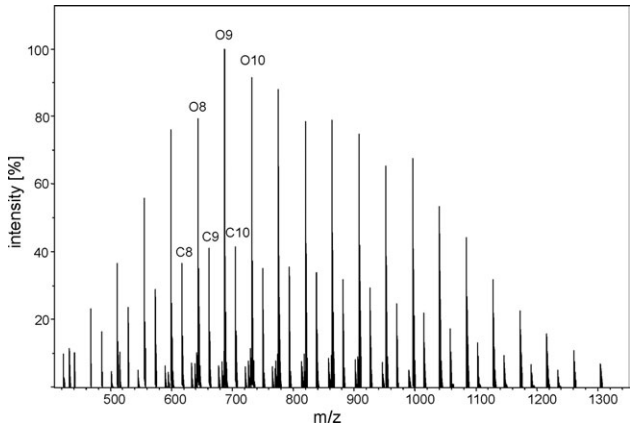

Figure 2. High-resolution, deconvoluted, ESI-Q-TOF mass spectrum of POE(10) oleyl ether (**7**).

ethoxylates are observed in the spectrum. Surprisingly, two distinct series are found. The more abundant series represents, as expected, the oleyl alcohol ethoxylates with a relative abundance of 70%. This series is labeled O(*n*), where *n* stands for the number of ethylene oxide units in the molecule. Accordingly, the spacing of the peaks in the O-series is 44.0262 amu, corresponding to C_2H_4O. Peaks correlating to oleyl ether ethoxylates ranging from O4 to O23 are found. Their distribution maximum lies at around nine ethylene oxide units (the peak labeled with O9), which is approximately consistent with the formula POE(10) oleyl ether (**7**). However, a second species of ethoxylated molecules with a relative abundance of 30% is observed, the C-series. The C-series also displays a spacing of C_2H_4O, but the peaks are shifted by *minus* C_2H_2 relative to the O-series. The hydrocarbon chain is therefore shorter by two carbon atoms and does not contain a double bond. The peaks of the C-series belong to the sodium adducts of cetyl alcohol ethoxylates (Figure 3). The contamination of commercially available POE(10) oleyl ether with cetyl ether ethoxylates was observed previously[22] and the authors of that study were equally surprised. To test whether this contamination is present only in our sample, a fresh specimen was obtained from Sigma-Aldrich. The time gap between the purchases of the two samples was 2 years. The mass spectrum of the new sample also showed the presence of two different fatty alcohol ethoxylates, 77% being oleyl alcohol ethoxylates and 23% cetyl alcohol ethoxylates. The maximum of the distribution of the oleyl ether ethoxylates lies at $n = 10$, which is consistent with the name POE(10) oleyl ether (**7**). We conclude that commercially available surfactant **7** is, in fact, a mixture of oleyl alcohol and cetyl alcohol ethoxylates. To test whether this holds true also for other oleyl alcohol ethoxylates such as surfactant **6**, a mass spectrum of this compound was also investigated (Figure 4). Surfactant **6** is interesting because it also displays a good anticalcification effect in PE. The mass spectrum shows once more two series of sodium adducts of ethoxylated fatty alcohols, one series is assigned to ethoxylates of oleyl alcohol, the other to ethoxylates of cetyl alcohol. The relative abundances are 73% for the oleyl and 27% for the cetyl alcohol ethoxylates. The distribution of the ethylene oxide units is intriguing. The formula POE(2) oleyl ether

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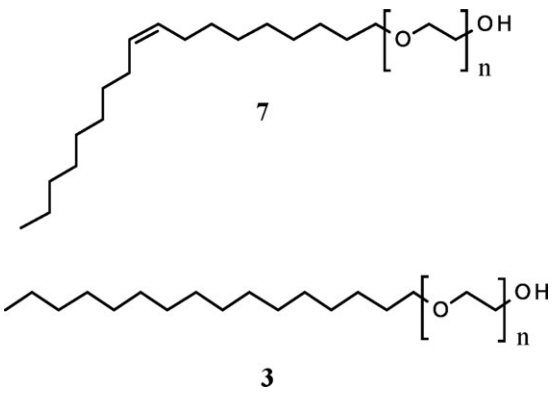

Figure 3. Above: POE(10) oleyl ether ($n = 10$) (**7**), below: POE(10) cetyl ether ($n = 10$) (**3**).

(**6**) for the commercial product implies that the most abundant ethoxylate should be the one with two ethylene oxide units. In contrast, the mass spectrum reveals that the most abundant oleyl alcohol ethoxylate is the one with five ethylene oxide units. Compound **6** should therefore correctly be named POE(5) oleyl ether. To confirm these results, a second sample was investigated by mass spectrometry. The second sample was directly ordered from Croda[15] and it was similarly 2 years younger than the first. Again, sodium adducts of oleyl (78%) and cetyl alcohol (22%) ethoxylates are observed in the mass spectrum. The maximum of the distribution of the oleyl alcohol ethoxylates lies at four ethylene oxide units, and therefore this compound should be referred to as POE(4) oleyl ether.

It is interesting to note that both new samples of surfactant **7** and surfactant **6** contain about the same amount (23 and 22%, respectively) of cetyl alcohol ethoxylates; whereas the old samples also contain comparable, but larger, amounts of cetyl alcohol ethoxylates (30 and 27%, respectively).

The question thus arises as to which component of surfactant **7** or surfactant **6** is responsible for the anticalcification efficiency. Is it the main component, the oleyl alcohol ethoxylates, or the minor component, the cetyl alcohol ethoxylates? This question can be answered because cetyl alcohol ethoxylates have also been tested for their anticalcification ability. POE(2) cetyl ether (**2**) and POE(10) cetyl ether (**3**) display no anticalcification efficiency in PE (Table II). It can therefore be concluded that the active anticalcification ingredients in surfactant **6** and surfactant **7** are the oleyl alcohol ethoxylates.

The third additive displaying good antiscaling efficacy in the laboratory tests was the PE-*b*-PEG **11**. This compound was also investigated by ESI mass spectrometry. The spectrum reveals that compound **11** is a complex mixture, with many signals observed. The intensities of the signals are roughly described by a bell-shaped profile, having its maximum at around 800 amu. It is concluded that PE-*b*-PEG **11** not only has PEG chains of varying lengths, but the PE chains also differ in size. This feature gives rise to a spectrum which is difficult to interpret. It is not possible to identify the species which are responsible for the anticalcification feature.

An attenuated total reflection infrared spectrum (ATR-IR) of surfactant **7** is shown in Figure 5. The strongest absorption band is at 1100 cm^{-1}.This band is attributed to the asymmetric stretch vibration of the C[sbond]O[sbond]C moieties of the PEG part of the molecule.[23] The PE matrix, on the other hand, shows only weak absorption at that wavelength (Figure 6, above). It should, therefore, be possible to observe the adsorption of the ether moieties in mixtures of surfactant **7** with PE. Figure 6 (below) shows an ATR-IR spectrum of a blend of 4% surfactant **7** with PE. An arrow marks the position of the band stemming from additive **7**. The absorption maximum of the ether moieties is slightly shifted to 1114 cm^{-1}, but still visible. The penetration depth of the IR light into the sample is typically between 0.5 and 2 μm, with the exact value determined by the wavelength, the angle of incidence, and the indices of refraction for the ATR crystal and the medium being probed.[24] Therefore, bulk properties of the plastic samples are obtained rather than surface features. Nevertheless, it is possible to correlate the amount of additive **7** in the matrix with the intensity of the signal at around 1100 cm^{-1}, and this correlation is shown in Figure 7. To obtain a normalized value, the maximum of the absorbance of the ether moieties at around 1100 cm^{-1} is

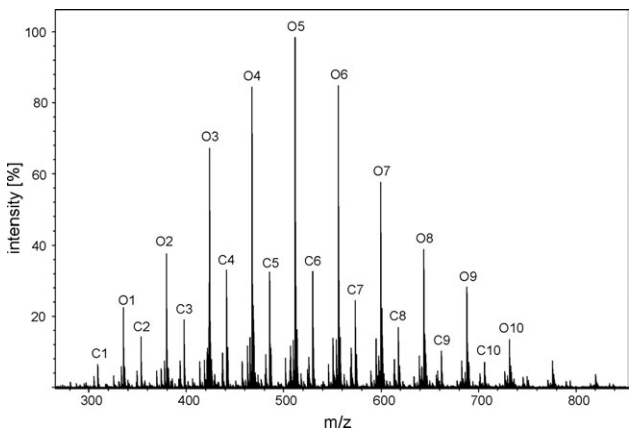

Figure 4. High-resolution ESI-Q-TOF mass spectrum of POE(2) oleyl ether (**6**).

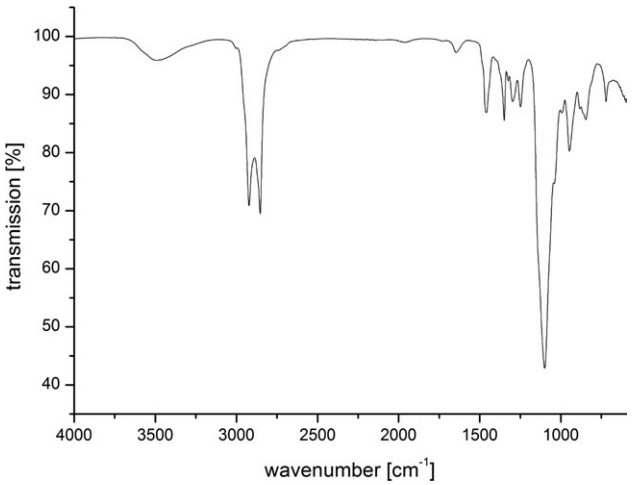

Figure 5. ATR-IR spectrum of POE (10) oleyl ether (**7**).

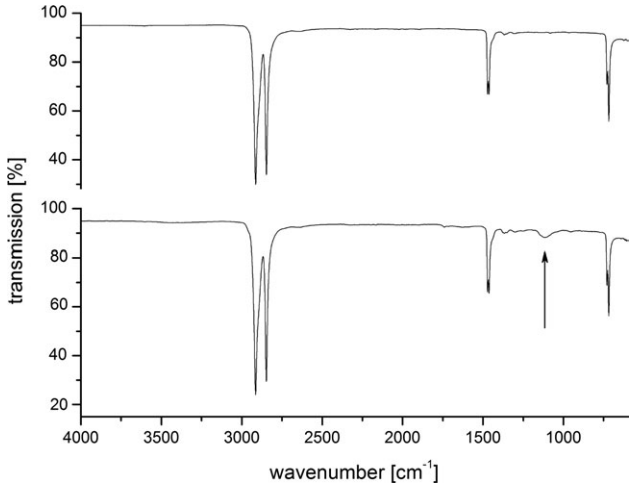

Figure 6. Above: ATR-IR spectrum of PE; below: ATR-IR spectrum of PE containing 4% POE (10) oleyl ether (**7**). The arrow indicates the band stemming from additive **7**.

divided by the absorbance of the PE matrix at 1472 cm^{-1}. (This absorbance is caused by the CH_2 deformation vibration[23] of the PE and its intensity is assumed to be constant). A dimensionless absorbance ratio is thus obtained, and is plotted against the additive content of the mixture. It is found that the higher the concentration, the stronger the absorbance ratio. A linear fit is also displayed. The linear regression fits the data quite well, considering the small absorbance ratios. The correlation coefficient of the linear fit is 0.953. The deviation of the measured data from the linear trend is presumably owing to part of the already minute quantity of the additives being lost to surfaces within the compounder.

Another observation is that at a concentration of 0% additive **7** there is still a positive value of absorbance ratio. This offset is caused by spurious absorption of the PE matrix at around 1100 cm^{-1}.

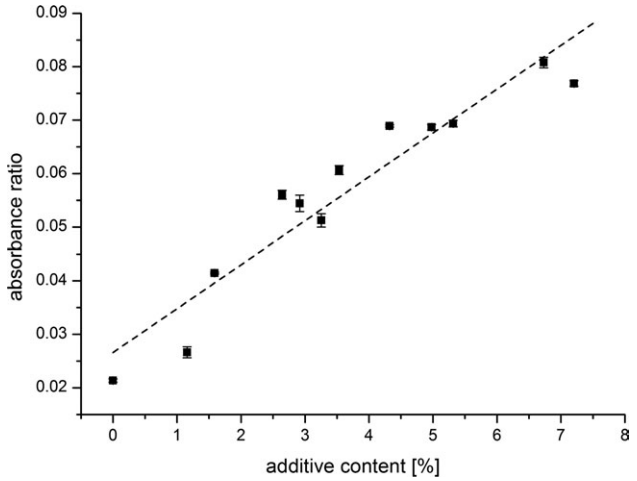

Figure 7. Infrared absorbance ratio against additive concentration for 12 different samples of PE containing various amounts of POE (10) oleyl ether (**7**).

The above analysis shows that because of the linear correlation between IR absorption and additive concentration, IR spectroscopy is a useful tool for quality control of the PE blends.

Water pipes, sanitary installations, and other water distribution systems are continuously in contact with water. A lime repellent material, therefore, has to be durable with respect to the long exposure time to water. In the best case, the efficiency against scaling should be retained for a system's lifetime. As it is very time consuming to test the stability of our lime repellent PE material under ambient conditions, we performed shorter, but tougher tests. Plates similar to the ones shown in Figure 1 were employed. They contained 4% of surfactant **7** and were exposed to the conditions described below for 21 days, after which their efficiency against scaling was investigated.

- Hot water at 50°C
- Hot water at 70°C
- Hot water at 70°C, pH 3
- Hot water at 70°C, pH 9
- Chlorinated water, 1 ppm, room temperature

The samples were first exposed to the challenging conditions, cleaned, and then calcified in the test rig. After calcification, visual inspection of the plates showed no calcium carbonate deposition; hence, this material is conclusively stable over the short-term intense tests described above. Subsequently, longer tests were conducted. Two batches of PE plates containing 4% surfactant **7** were subjected to 70°C warm water in an autoclave under air pressure for 2000 h. Then, the two batches were calcified. Weighing the amount of calcium carbonate deposited yielded 17 ± 5% ($n = 6$ samples) for the first batch, and ~0% ($n = 5$ samples) for the second batch calcification relative to an untreated ABS reference. Although the two batches differ significantly, it is concluded that the stability under the conditions tested is good to very good, and it is anticipated that the material will display an even longer efficiency against scaling if exposed to water at room temperature.

CONCLUSIONS

Our goal is to inhibit the calcification of polymer surfaces without the use of chemicals or energy. The approach is to make surfaces to which calcium carbonate crystals do not bind. We previously reported that PEG at surfaces inhibits scaling; presumably by forming a liquid-like layer to which calcium carbonate crystals do not adhere. The challenge is to find a simple, cheap, and reliable method to attach PEG to the surface of the polymer. Here, we show that for PE this task can be accomplished by the use of copolymer additives. The 12 additives investigated have the structure PE-*b*-PEG. Three thereof (two nonionic surfactants and a specific PE-*b*-PEG) display good antiscaling activity when compounded into the PE at a concentration of 4.8%. Plates of PE, blended with 4% POE(10) oleyl ether, were produced and it was found that they were not calcified when exposed to hard water, contrary to the unblended PE plates.

High-resolution ESI mass spectra of the three copolymers revealed that all are mixtures, contradicting the information from the suppliers. It is concluded, however, that for the two active,

nonionic surfactants the effective ingredients are the oleyl ether ethoxylates. ATR-IR was used to analyze the blends of PE with POE(10) oleyl ether, and it was shown that the absorption of the ether moieties at around 1100 cm^{-1} can be correlated to the additive concentration. Finally, stability tests show that the anti-calcification property of the PE blends with POE(10) oleyl ether was preserved when exposed to water at 70°C for at least 2000 h.

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AUTHOR CONTRIBUTIONS

K. S. was responsible for the selection and analysis of copolymers and blends and drafted the article. R. S. compounded the strands, performed the calcification measurements and evaluations, and critically read and approved the article. R. W. produced the PE plates with additive, interpreted the calcification results, and revised the article and M. H. designed the research and critically reviewed the manuscript.

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