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Analysis of Cell-Stabilizing Additives in Low-Density Polyethylene Foams Using Low-Frequency Dielectric Spectroscopy

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ABSTRACT: Addition of low amounts of additives is necessary to guarantee dimensional stability of low-density flexible polyethylene foam after extrusion. It is expected that the additives form a layer on the foam cell walls. However, the physical phenomena responsible for the stability improvement are not well understood. Using low-frequency dielectric spectroscopy, we show the occurrence of interfacial polarization in these low-density polyethylene foams. We hypothesize and prove that a stabilized low-density, closed cell polyethylene foam can be regarded as a three-phase system with a polyethylene matrix forming the cell walls, a filler being the gas phase, and an intermediate additive layer. At elevated temperatures the additive layer will become conductive resulting in interfacial polarization, thereby excluding the entire filler volume from the electrical field. This is reflected in an increase of the dielectric constant of the foam from initially 1.0 to about 300 at the melting point of the additive. The frequency-independent position of the peaks suggests that the additive layer is crystalline.

Introduction

In a multicomponent, multiphase macromolecular system, the interface between the different phases affects the macroscopic properties significantly. However, experimentally such interfaces are difficult to assess, and their physical nature as well as their effect on the macroscopic materials properties remains a matter of laborious experimentation and extensive reasoning. For a high porosity polymer foam, we aim to demonstrate that dielectric spectroscopy allows direct measurements of the demixing and migration of a low molecular weight additive from the bulk of a polymer lamellae toward its surface. Although applied only to polymeric foams, the methodology presented may be as well applied to macromolecular systems comprising polymers, fillers, and compatibilizers.

Low-density foams are frequently used for insulation applications. Physical expansion of a blowing agent such as isobutane or carbon dioxide during the melt extrusion process results in closed-cell, honeycomb-like morphologies having an extremely high porosity and a density of $\rho < 50$ kg/m^3. The addition of low molecular weight additives, in general fatty acids, is essential to obtain a dimensionally stable low-density polyethylene foam. Dimensional instability stems from a rapid permeation of the physical blowing agent out of the closed-cell structure, while only slow counterpermeation of air into the foam occurs. This results in a rapid initial shrinkage followed by a slow expansion. It is believed that the working mechanism of these low molecular weight additives is based on phase separation with the additive migrating to the foam lamella surface. We hypnotize the additives to form a (partly) crystalline layer at the surface of foam lamella, thereby reducing the gas flux of the blowing agent out of the foam.[1] However, because of the small dimensions (layer thickness up to 20 nm) and heterogeneity of these foam systems, common techniques like scanning electron microscopy, infrared spectroscopy, and X-ray diffraction are not suitable to characterize these additives inside polymeric foams. Many questions remain with respect to the morphology (amorphous vs crystalline) and the thickness of the layer.

It is well-known that the additives used to increase dimensionals stability exhibit also antistatic properties. Antistatic agents are chemicals that provide a conductive coating on a polymer surface so that static charges can leak off.[2,3] The conductivity of the surface layers can cause interfacial polarization when they are present in a nonconductive polymer matrix, e.g., a foam. Interfacial polarization causes the dielectric constant to increase substantially. The work presented below makes use of this phenomenon and presents experimental results, establishing dielectric spectroscopy as a sensitive technique to study distribution and nature of polar additives in polymer foams.

Background

Applying an electrical field can polarize a material. The polarizability of a material is given by its relative dielectric constant ϵ_r. This is the ratio between the permittivity of the examined material and the permittivity of free space ϵ_0 (8.85 pF/m). Equation 1 shows the relative dielectric constant, expressed in its complex form $\epsilon^*(\omega,T)$:

$$\epsilon^*(\omega,T) = \epsilon'(\omega,T) - j\epsilon(\omega,T) \qquad (1)$$

with $\epsilon^*(\omega,T)$ the complex dielectric constant, $\epsilon'(\omega,T)$ the real part of the dielectric constant (capacitive compo-

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nent) or *dielectric constant*, and $\epsilon''(\omega,T)$ the imaginary part of the complex dielectric constant or *loss index*. The storage and dissipation of field energy are expressed by the dielectric permittivity or ϵ' and the loss factor or ϵ'', respectively. Both dielectric permittivity and loss factor are functions of the frequency of the alternating electric field and the temperature.

The storage of field energy is a capacitive effect, caused by the polarizability of the material. The time related to the dynamics to reach a state of complete polarization is referred to as the relaxation time τ. Three polarization mechanisms can be distinguished: (1) Electric/atomic polarization: the displacement of binding electrons or atoms from their equilibrium position on a molecular level (induced dipoles). This process is very fast and can be regarded as frequency independent. (2) Dipole orientation: the orientation of permanent dipoles along electric field lines. This process has typical relaxation times of $10^{-6}-10^{-8}$ s. (3) Interfacial or Maxwell–Wagner polarization: a macroscopic buildup of charges at internal interfaces. This occurs when two materials with dissimilar conductivities are subjected to an electric field. This process is relatively slow ($\tau >$ 1 s) and can be investigated by low-frequency dielectric spectroscopy. The mentioned relaxation times are not absolute; they depend on temperature. However, they indicate the strong increase going from electric/atomic to MWS polarization.

The dissipation of field energy is irreversible, and the main mechanisms are related to the following: (a) The conductivity of the material: field energy will dissipate as heat; this process takes place only at low frequencies. (b) Frictional losses: the polarization effects (1–3) can cause atomic/molecular displacement, dissipating field energy as heat of friction.

Heterogeneous Systems. Numerous authors have described the dielectric behavior of heterogeneous systems. The approach of Sillars,[4] Wagner,[5] and Maxwell–Garnett[6] was limited to rather small filler volume fractions (<30 vol %). Böttcher,[7] Looyenga,[8] and Bruggeman[9] extended the equations to higher filler volume fractions. Bruggeman derived the following relation

$$\frac{\epsilon_c^* - \epsilon_2^*}{\epsilon_1^* - \epsilon_2^*}\left(\frac{\epsilon_1^*}{\epsilon_c^*}\right)^n = 1 - \varphi_2 \qquad (2)$$

with $\epsilon_{1,2,c}^*$ the complex dielectric constant of the polymer, filler, and composite, φ_2 the volume fraction component 2, and n the shape factor, correcting for the shape of the inclusion.

For a composite, e.g., a foam, consisting of spherical inclusions ($n = {}^1/_3$) of a nonconductive filler material (blowing agent) embedded in a nonconductive matrix material (polymer), both having a frequency-independent dielectric constant, eq 2 can be simplified to eq 3, giving the dielectric constant of the composite:

$$\frac{\epsilon_c - \epsilon_f}{\epsilon_m - \epsilon_f}\left(\frac{\epsilon_m}{\epsilon_c}\right)^{1/3} = 1 - \varphi_2 \qquad (3)$$

with ϵ_c the dielectric constant of the composite, $\epsilon_{m/f}$ the dielectric constant of the matrix/filler, and φ_2 the volume fraction of filler material.

A low-density polymer foam can be considered as an extreme case of a heterogeneous system. The polymer is the continuous phase with a volume fraction of less than 0.05. The gaseous component, consisting of air, the blowing agent, or a mixture of these, is the filler with a volume fraction larger than 0.95. Depending of the volume fraction, the dielectric constant is directed toward the dielectric constant of the blowing agent. It was shown by Krause et al.[10] that incorporation of 40 vol % of blowing agent in polyimide films reduced the dielectric constant of the nanoporous foam into the ultralow k ($\epsilon < 1.8$) region. In our case, a low-density, macrocellular foam, this results in a dielectric constant of the composite resembling that of the blowing agent.

Heterogeneous Systems with Conducting Interlayer. In contrast to the two-phase system comprising the nonconductive filler in a nonconductive polymer, a three-phase system with a conductive interlayer may show surprising characteristics. A conductive interlayer can turn the nonconductive dispersed phase into an apparently conducting phase, excluding the filler volume from the electrical field. In the case of spherical filler particles, such as glass beads with adsorbed water as conducting interlayer, Steeman[11] has derived the following equation for low limiting frequencies, $\omega \rightarrow 0$ (situation of complete polarization):

$$\epsilon_s = \epsilon_m\left(\frac{1 + 2\varphi_f}{1 - \varphi_f}\right) \qquad (4)$$

with ϵ_s the dielectric permittivity of the composite for $\omega \rightarrow 0$, ϵ_m the dielectric permittivity of the matrix, and φ_f the filler volume fraction.

Because of the exclusion of the filler volume by the conductive interlayer, the dielectric permittivity of the composite is simply a function of the dielectric permittivity of the matrix material and the filler volume fraction. From a dielectric point of view, the system is then reduced to a two-phase system consisting of a nonconducting matrix and a filler with an infinite dielectric permittivity. Steeman's equation predicts an asymptotic increase of the dielectric permittivity of the composite with increasing filler volume fraction, and this has been validated for glass beads ($\varphi_f < 0.20$) in a polymer matrix in the presence of water. Equation 4 is based on a model for spherical inclusion and is thus limited to a maximum filler degree equal to the percolation threshold ($\varphi_{max} = 0.52$). In the following we will present experimental evidence that an increase in ϵ_s can also be observed with higher filler volume fractions ($\varphi_f > 0.95$) for a low-density polyethylene foams with a conductive interlayer of the cell walls. In this work we will use the rise in dielectric constant, stemming from the presents of the interlayer forming additive, to reflect on its physical properties. The reader is reminded that eq 4 is not defined for such filler degrees. In a subsequent article, we will present a model allowing to predict ϵ_s at these high filler degrees. This theoretical analysis uses equivalent circuits to predict the rise in ϵ. In fact, it will show that eq 4 is sufficiently accurate to be used beyond the percolation threshold. Hence, we will use eq 4 as a tool to estimate ϵ_s, well knowing that it is used outside its valid boundary conditions.

Experimental Section

Setup. The dielectric measurements were performed on the dielectric setup at DSM Research, Geleen, The Netherlands. A schematic representation is shown in Figure 1. The parallel plate electrode setup is cooled and heated with a nitrogen gas flow. The Solartron 1260 frequency response analyzer (FRA) applies a sinusoidal voltage with a frequency between 50 mHz

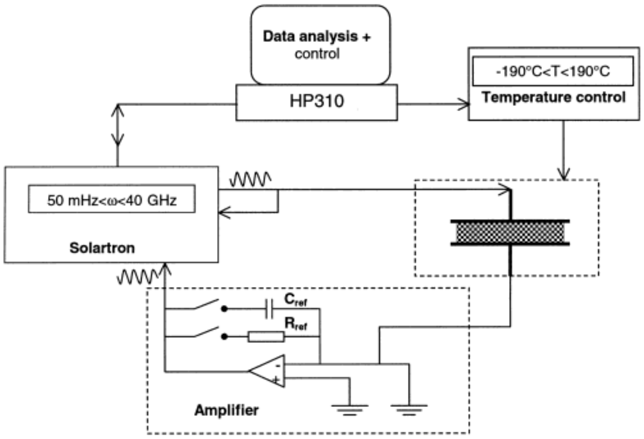

Figure 1. Schematic representation of the dielectric spectrometer.

and 40 MHz and an amplitude of $10V_{eff}$ to the upper plate. The resulting current is amplified by a dielectric electrometer, built by TNO, The Netherlands. The FRA measures the phase and amplitude relations between the applied signal and the obtained sample current. From these, the dielectric properties can be calculated. After each complete frequency scan the temperature was increased by a step of 2 °C. The time to perform a complete frequency scans lasts several minutes.

Materials. To comply with the circumstances during foam production, all chemicals used were commercial grade. Low-density polyethylene (LDPE), Stamylan 2601TX17 from DSM (926 kg m^{-3}), was blended with glycerol monostearate (GMS) Atmer 1013, stearyl stearamide (St.St) Kenamide S180, dodecylamine, or an ethoxylated amine (GAn) Atmer 7105. The additives contain impurities, e.g., ions, which will provide means for conduction as the temperature of the additive rises. The polyethylene and additives were kindly supplied by DSM. The resulting compositions were foamed from the melt with the use of a two-stage extruder using carbon dioxide or isobutane as physical blowing agent. The resulting foams have cell diameters of approximately 450 μm and cell walls with a thickness of 4−5 μm. All foaming experiments were conducted by NMC sa (BE). The composition and the density of the investigated foams are listed in Table 1.

The produced foams were stored in ambient conditions, awaiting experimental preparation. The foam was provided in a rod configuration with a diameter of approximately 3 cm. Samples were used with a thickness of approximately 0.3 cm, taken from the cross section of the rod. All reported values are corrected for the effective sample surface and thickness; the latter was determined from the raw experimental values

A blend containing 4 wt % of GMS in polyethylene was prepared with a miniextruder. Compression molding of this blend was done at 160 °C and 35 kN to produce a 100 μm thick film. The film was annealed for 1 h at 83 °C to accelerate demixing of the additive and polymer.[1,12] To optimize the sample−electrode contact all samples were covered with a thin gold layer by sputtering, preventing electrode polarization. Dielectric spectroscopy was applied to both films and foams. Additionally, X-ray photoelectron spectroscopy was performed on the films and foams to verify the existence of the additive layer at the surface, and differential scanning calorimetry was performed to characterize the pure components.

Results and Discussion

Dielectric Spectroscopy. The dielectric properties of the pure components of the foams as well as their melting temperature are listed in Table 2.

Figure 2 shows the dielectric permittivity of an isobutane blown foam without additives as a function

Table 1. Composition and Density of Investigated Foams

sample	additive	structural formula	concentration [wt %]	ρ [kg/m^3]	blowing agent
1	none			31.4	i-C_4H_{10}
2	GMS	$C_3H_7O_3{-}C(O){-}C_{17}H_{35}$	1.5	38.4	CO_2
3	St.St.	$C_{17}H_{35}{-}C(O){-}N(H){-}C_{18}H_{37}$	1.5	31.9	i-C_4H_{10}
4	GAn	$(C_2H_5O)_2{-}N{-}C_{12}H_{25}$	1.5	39.0	CO_2
5	GMS/GAn	$C_{21}H_{25}{-}NH_2$	1.5/1.0	39.5	CO_2

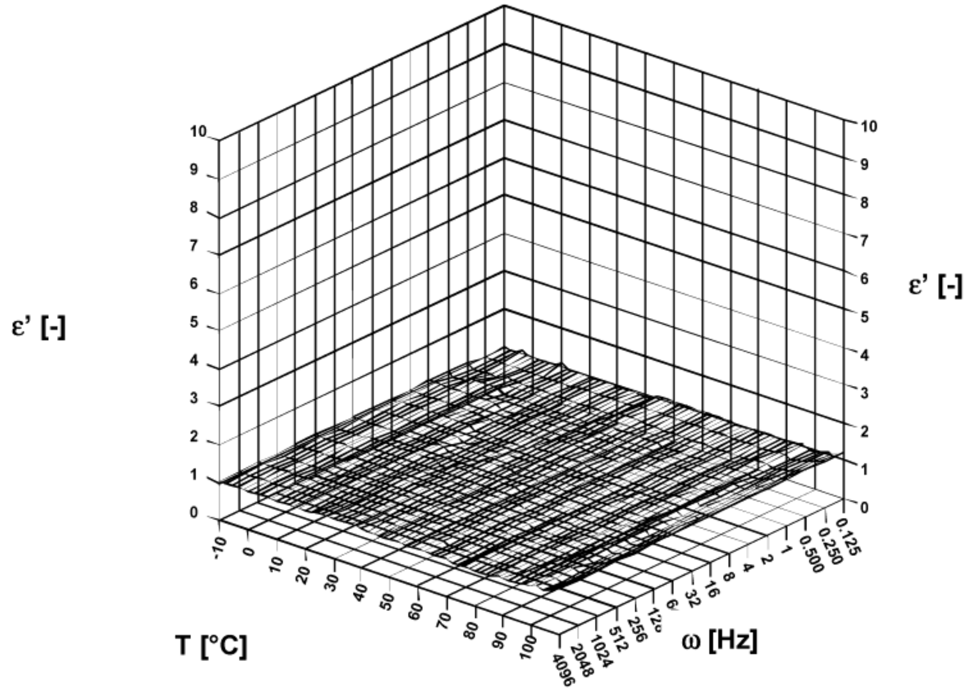

Figure 2. Dielectric permittivity of an isobutane blown polyethylene foam, without additives, as a function of temperature and frequency.

Table 2. Dielectric Permittivity and Melting Temperature, Determined with DSC, of the Pure Components

material	dielectric permittivity (ϵ')[13]	T_m(DSC) [°C]
polyethylene (PE)	2.3	112
isobutane	≈1.000	
carbon dioxide	1.00056	
glycerol monostearate (GMS)	4.84	68
stearyl stearamide (St.St)	not known	98
dodecylamine (dod)	3.07	16
ethoxylated amine (GAn)	not known	1.8

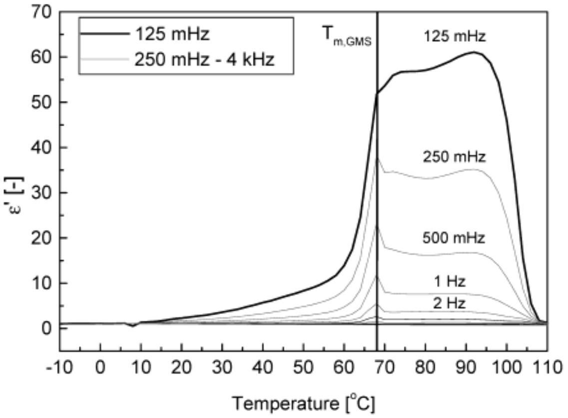

Figure 3. Dielectric permittivity (ϵ') of LDPE foam containing 2.0 wt % glycerol monostearate as a function of temperature and frequency.

of temperature (−10 to −110 °C) and frequency (125 mHz−4 kHz). Within these intervals no dependence of the dielectric permittivity on temperature or frequency was observed. This situation corresponds to a two-phase system, a polymer matrix filled with gas, as described by Bruggeman.[9] The numerical values of Table 2 substituted in eq 3 give a dielectric permittivity of the foam of 1.03. This is consistent with the measured values, which vary between 1.0 and 1.1. The loss index does not depend on temperature and frequency either within these intervals and is close to 0, indicating that there are no conduction or polarization losses. Table 2 also indicates that the composition of the cell gases is only of minor importance, since their dielectric values do not differ significantly.

The effect of an additive, present in the foam, becomes apparent in Figure 3, where the dielectric permittivity is plotted as a function of the temperature for different frequencies. A first change in the dielectric permittivity is observed at 20 °C. At this temperature the solid additive layer becomes slightly conductive. With increasing temperature the conductance of the additive increases further and leads to a stronger interfacial polarization. This polarization effect is most pronounced at the lower frequencies (<1 Hz), allowing the longest relaxation times. As there is still a significant increase of the measured maximum even at the very low frequencies, it is to be expected that a complete relaxation of the system is not reached (τ > 8 s).[14] This explains why the observed dielectric permittivity of 60 is considerably lower than the theoretically calculated value ($\epsilon' = 193$) using (4). At frequencies higher than 2 Hz the system is fully unrelaxed: the measured dielectric permittivity is now close to 1.03 and does not depend on either temperature or frequency, indicating that no interfacial polarization occurs.

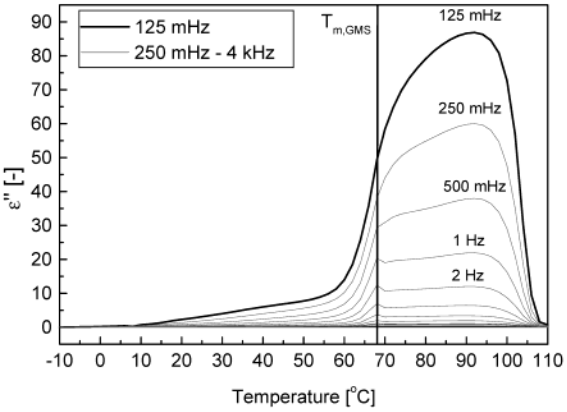

Figure 4. Loss index (ϵ'') of LDPE foam containing 2.0 wt % glycerol monostearate as a function of temperature and frequency.

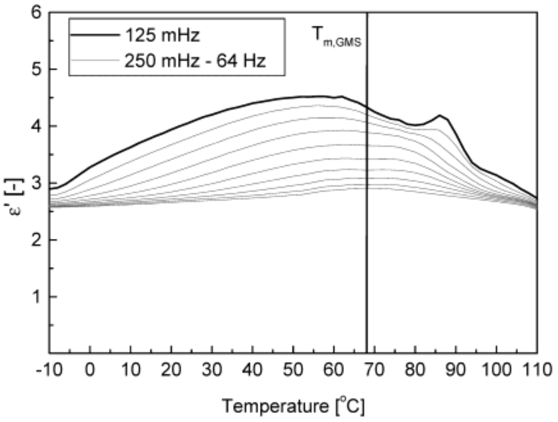

Figure 5. Dielectric permittivity of three stacked layers LDPE film containing 4 wt % glycerol monostearate as a function of temperature and frequency.

The melting point of glycerol monostearate is distinct (T_m = 68 °C) in all curves. At temperatures higher than the melting temperature a plateau is reached, which remains constant until 100 °C. The frequency-independent position of the onset of the plateau indicates a first-order phase transition. This transition can only stem from the solid−liquid transition of GMS, since in Figure 2 no transition is observed for the pure polymer. One may conclude that at this point the additive crystals at the polymer surface melt, thereby increasing the mobility of the conducting ions in this layer, resulting in the maximum interfacial polarization.

In Figure 4 the same behavior can be observed for the loss index. The phase transition of the additive, however, is less distinct at the lower frequencies. In the partly unrelaxed state, interfacial polarization causes dynamic conduction losses. In a subsequent paper, this hypothesis is verified by performing conductivity measurements on the pure additive.[14]

To compare these results with a system with a filler fraction equal to zero, we analyzed dense polyethylene films containing 4 wt % glycerol monostearate. To accelerate demixing of the additive and the polymer, the films were annealed.[1] Three films were stacked, thereby creating two internal surfaces. In this configuration one can assume the filler volume fraction (gas fraction) to be close to 0. The results of the dielectric experiments performed on these films are plotted in Figure 5. At very

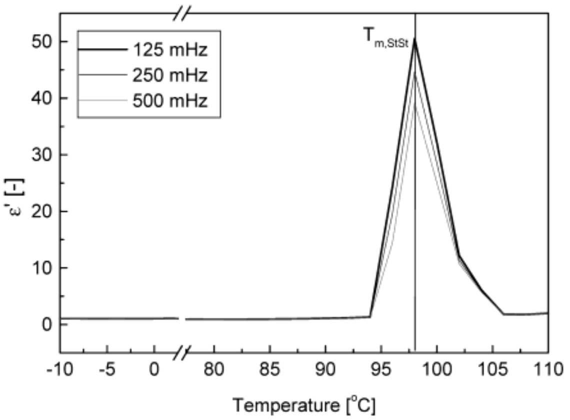

Figure 6. Dielectric permittivity of a polyethylene foam containing 2.0 wt % stearyl stearamide as a function of temperature at 125, 250, and 500 mHz.

low temperature or at high frequency the dielectric permittivity of the system has the value of 2.6, which is close to the calculated dielectric permittivity a composite consisting of stacked layers of pure GMS and PE, with the total thickness of the GMS layers being 4% of the total thickness. At temperatures $T > -10$ °C and frequencies $\omega < 64$ Hz the dielectric permittivity starts to increase to a maximum of approximately 4.5. So also in this configuration with internal additive layers, the dielectric permittivity increases, however, to a significantly lesser extent than in the case of the foams. The dielectric permittivity increases only to a value of 5, whereas in the case of the investigated foams the dielectric permittivity was close to 70 (and even 193 according to theory, eq 3 with $\phi_f = 0.965$). This shows clearly the influence of the high filler volume fraction, which in the case of a thin conducting interlayer is completely excluded from the electric field. In this case the foam is reduced to a pseudo-two-phase system: a nonconductive polyethylene matrix with a conducting filler phase.

The small peak appearing between 80 and 90 °C is caused by impurities in the GMS. HPLC analysis has indicated the presence of up to 35% substituted glycerol impurities similar to GMS, primarily glycerol monopalmitate. Thorough analysis of Figure 3 shows that this peak is also present in the dielectric constant of the foam. Above 100 °C, the dense PE/GMS films show the same behavior as the foams. The dielectric permittivity drops to its original value for all frequencies. We will show in a subsequent article that an increased solubility of the additive with temperature leads to a redissolving of the additive in the polymer, causing the interfacial polarization to vanish.

Additionally, dielectric experiments were performed on foams containing three other additives. First, a foam that contained 1.5 wt % stearyl stearamide was prepared using isobutane as blowing agent and with a final density of 31.9 kg/m^3 (Figure 6). Also, the melting point of this additive is clearly observed at 98 °C. In this case the system again is not completely relaxed, possibly explaining the relatively low value of the dielectric permittivity. Directly after the maximum is reached, the dielectric permittivity starts to decrease, whereas in the case of glycerol monostearate a plateau is observed. In both cases, however, the dielectric permittivity drops to the original value. Two hypotheses can be proposed to explain this behavior. (1) Melting of the LDPE destroys the foam structure, resulting in higher densities/lower filler volume fractions and consequently a lower dielectric permittivity (eq 3). (2) At higher temperatures the solubility of the additive in the amorphous phase of polyethylene increases. This combined with a lower crystallinity of the polymer at higher temperatures can reduce the additive layer thickness to be close to zero.[15] In this case the system is reduced to a system similar as in Figure 2.

(1) Melting of LDPE does not occur before 110 °C, whereas the decrease of the dielectric permittivity does. The melting of the polyethylene matrix takes place between 110 and 120 °C. In this interval the dielectric permittivity increases from around 1.0−1.1 to 2.3, the intrinsic value of the dielectric permittivity of LDPE. Collapse of the foam morphology was only observed at temperatures well above the temperature associated with the decline of the dielectric permittivity. Hence, this rejects hypothesis 1.

(2) Recent modeling of the dielectric response of foams by an electrical circuit analysis clear supports this hypothesis.[14,15] The model requires as input parameters (a) the geometry of an elementary cell, (b) the additive layer thickness, (c) the thermal characteristics of the additive, and (d) the temperature-dependent solubility of the additive in the polyethylene. Even though the diffusion coefficients of the additives may be low at room temperature, resolubilization into the lamellae occurs at elevated temperatures, and diffusion equilibrium is reached within the time necessary to perform a frequency sweep.

With two other additives, however, we did not find this significant increase of the dielectric permittivity. In dielectric experiments on foams containing 1.5 wt % of an ethoxylated amine (GAn) or dodecylamine, no dependence of the dielectric permittivity or loss index was observed on the measured temperature and frequency interval. The dielectric behavior of these foams was exactly the same as the foam containing no additives (Figure 2). Two explanations can be given for this behavior: first, these additives are not present at the surface of the cell walls or, second, that these additives form a poorly conducting interlayer. However, this latter explanation is unlikely because the additives used are liquids at room temperature: the melting temperatures T_m are 2 and 16 °C, respectively. In general, the liquid state has a relatively high conductivity compared to the solid state, due to larger ion mobility in the liquid. In a subsequent paper this hypothesis will be verified by doing conductivity measurements on the pure additives and by estimating the solubility of the additives in polyethylene using a group contribution method.

Figure 7 shows the dielectric permittivity of a foam containing a mixture of 1.5 wt % glycerol monostearate and 1.0 wt % of an ethoxylated amine plotted as a function of temperature and frequency. The addition of GAn increases the maximum value of the dielectric permittivity (260), which is already higher, even at 125 mHz, than the theoretically expected maximum (235). The decreasing distances between curves when going to lower frequencies indicate that the system is closer to complete relaxation. The presence of GAn may lead to a thicker interfacial layer, either by the presents of GAn in the layer or a facilitation of the demixing kinetics of LDPE and GMS by GAn.[3,16]

X-ray Photoelectron Spectroscopy. To verify whether the additive layer is present on the surface of

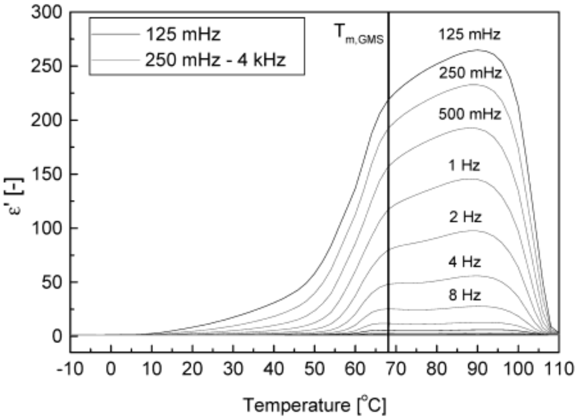

Figure 7. Dielectric permittivity of a polyethylene foam containing 1.5 wt glycerol monostearate and 1.0 wt % of and ethoxylated amine as a function of temperature and frequency.

the cell walls, X-ray photoelectron spectroscopy (XPS) was performed on films and foams. XPS has a typical penetration depth up to 10 nm, which is suitable to characterize the surface composition of the foams. The experiments were carried out on nonpretreated simple cross sections of foam rods, whereby the XPS was focused on the inner part of the cell rather than on the cross section of the cell walls, thereby characterizing the surface composition of the internal cell walls. The results of these experiments are listed in Table 3.

Table 3 shows that the surface composition of LDPE film and foam without additives is in good agreement with the expected composition. The low concentration of oxygen at the surface can be assigned to oxidation of the surface, which can introduce oxygen up to levels of 1 atomic %.[17] The film, which contains 1.5 wt % glycerol monostearate, shows good agreement between measured and expected value (14 vs 16 atomic % oxygen). The corresponding foam has a lower atomic % oxygen. We have two explanations for this observation: (a) the penetration depth of XPS in this system is higher than the layer thickness, thereby also detecting LDPE underneath this layer, lowering the relative amount of oxygen detected, or (b) low molecular weight LDPE or LDPE waxes can segregate from the polymer lamella into the interlayer, hence lowering the percentage of atomic oxygen at the surface.

The observed shift of the oxygen peak (from 285 to 287 eV) indicates double-bonded oxygen, as present in glycerol monostearate. From these arguments one may conclude that in both systems a surface layer is present, containing mainly glycerol monostearate.

Films and foams containing 1.5 wt % of an ethoxylated amine did not show the presence of the additive at the surface. This observation fully supports the results, which were obtained with dielectric spectroscopy. The (low) atomic % oxygen can again be assigned to the oxidation of the surface.[17] No nitrogen was detected at the surface, whereas almost 5% was expected in the case of a fully covered surface.

In the foam with a mixture of glycerol monostearate and an ethoxylated amine, oxygen can be found as well on the surface of the cell walls. The amount of oxygen and the shift of peak indicate that glycerol monostearate is present at the surface. The absence of a nitrogen peak again demonstrates that no ethoxylated amine is present at the surface of the cell walls. This supports the hypothesis that when using the mixture of GMS/GAn, GAn does not migrate to the surface. However, as the dielectric signal of the foam is significantly increased compared to the use of pure GMS, this supports the hypothesis that the GAn facilitates the demixing of GMS and polyethylene.

Conclusions

Low-frequency dielectric spectroscopy is a method to prove the presence of an additive layer at the surface of the cell walls of a closed cell, low-density polyethylene foams. The important condition to be fulfilled is that the additive is conductive in order to establish interfacial polarization. This effect occurs in the case of low frequencies in which the dielectric permittivity (ϵ') of a foam may increase from 1.03 (no interfacial polarization) up to 350 (fully relaxed interfacial polarization). Dynamic conduction losses during the interfacial polarization also show a strong increase of the loss index (ϵ'') from approximately 0 in the unrelaxed situation to about 40 in the fully relaxed situation.

Two of the four investigated additives, glycerol monostearate and stearyl stearamide, showed a strong increase in both the dielectric permittivity and the loss index of the foam, implying the presence of a surface layer at the cell walls. The frequency-independent positions of the peaks suggest the melting of a (partly) crystalline character of this surface layer. Because of migration of this layer into the polymer at 90−100 °C, induced by the increasing solubility of the additive in the polymer, the interfacial polarization reduces toward its original low value.

A third additive, an ethoxylated amine, does not increase the dielectric permittivity of the foam. This is caused by the fact that the ethoxylated amine is not present at the surface of the cell walls. The solubility of this additive in polyethylene is assumed to be higher than the added amount, which means that the additive will be present in the bulk instead of the surface. Obviously, *only* the presence of the additive at the *surface of the cell walls* is responsible for the large increase of the dielectric permittivity.

The combination of the ethoxylated amine with glycerol monostearate increases the dielectric permittivity to 350. It seems that the presence of the ethoxylated amine accelerates demixing of the polyethylene

Table 3. Surface Composition (in %) of LDPE Films and Foams As Determined with X-ray Photoelectron Spectroscopy

additive	composition c [wt %]	in theory[a] C 1s	O 1s	N 1s	film[b] C 1s	O 1s	N 1s	foam C 1s	O 1s	N 1s
no additive		100	0	0	99.3	0.5	≈0	99.3	0.5	≈0
GMS	1.5	84	16	0	86.0	14.0	≈0	92.1	7.9	≈0
GAn	1.5	73.7	9.5	5	99.5	0.4	≈0	99.7	0.3	≈0
GMS/GAn	1.5/1.0	74.7	13.4	2	85.1	13.4	≈0	97.2	2.7	≈0

[a] In case of a complete demixed system and additive layer completely covering the cell wall surface. [b] Annealed to accelerate demixing.

and glycerol monostearate or produces a more conducting surface layer.

Results obtained with X-ray photoelectron spectroscopy verify these results. Glycerol monostearate was found to be present at the surface of the cell walls. The ethoxylated amine, however, could not be detected. Also, in the foam with both glycerol monostearate and the ethoxylated amine only glycerol monostearate was present at the surface.

List of Symbols

$\epsilon^*(\omega,T)$	complex dielectric constant [−]
$\epsilon'(\omega,T)$	real part of the dielectric constant or dielectric permittivity [−]
$\epsilon''(\omega,T)$	imaginary part of the complex dielectric constant or loss index [−]
ϵ_c	dielectric constant of the composite [−]
ϵ_f	dielectric constant of the filler [−]
ϵ_m	dielectric constant of the matrix [−]
ϵ_s	dielectric constant of the composite, $\omega \to 0$ [−]
ω	angular frequency [Hz]
φ_f	volume fraction filler material [−]
c	concentration [wt %]
n	shape factor [−]
T_m	melting temperature [°C]

References and Notes

(1) Bouma, R. H. B.; Nauta, W. J.; Arnauts, J. E. F.; Van den Boomgaard, Th.; Steuten, J. M.; Strathmann, H. *J. Appl. Polym. Sci.* **1997**, *65*, 2679.
(2) Polzhofer, K.; Lehmann, H. *Angew. Makromol. Chem.* **1974**, *36*, 145.
(3) *Plastic Additives Handbook*, 5th ed.; Zweifel, H., Ed.; Hanser Publ: Munich, 2001; p 629.
(4) Sillars, R. W. *J. Inst. Electr. Eng.* **1937**, *80*, 378.
(5) Wagner, K. W. *Arch. Electortechn.* **1914**, *2*, 371.
(6) Maxwell Garnett, J. C. *Philos. Trans. R. Soc. London* **1904**, *203*, 385.
(7) Böttcher, C. J. F.; Bordewijk, P. *Recl. Trav. Chim.* **1945**, *64*, 47.
(8) Looyenga, H. *Physica* **1965**, *31*, 401.
(9) Bruggeman, D. A. G. *Ann. Phys. (Leipzig)* **1935**, *24*, 636.
(10) Krause, B.; Koops, G. H.; Van der Vegt, N. F. A.; Wessling, M.; Wubbenhorst, M.; Van Turnhout, J. *Adv. Mater.* **2002**, *14*, 1041.
(11) Steeman, P. A. M.; Maurer, F. H. *J. Colloid Polym. Sci.* **1990**, *268*, 315.
(12) Park C. P. U.S. Pat. 4,640,933, 1987.
(13) *Handbook of Chemistry and Physics,* 62th ed.; CRC Press: Boca Raton, FL, 1981.
(14) Barsema, J. N.; Bostoen, C. L.; Jansen, R. H. S.; Mulder, M. H. V.; Nauta, W. J.; Steeman, P. A. M.; Wessling, M., to be submitted for publication.
(15) Moisan, J. Y. *Eur. Polym. J.* **1980**, *16*, 979, 989.
(16) Pfahler, G. *Kunststoffe* **1987**, 77.
(17) Olde Riekerink, M. B.; Terlingen, J. G. A.; Engbers, G. H. M.; Feijen, J. *Langmuir* **1999**, *15*, 4847.

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