Migration of quaternary ammonium cations from exfoliated clay/low density polyethylene nanocomposites into food simulants

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Additional experimental procedures and discussion

A. Film manufacture

OMMT/PE-g-MA/LDPE. Preparation of these materials involved a two stage mixing process. In the first step, a 1:3 (by mass) mixture of OMMT/PE-g-MA masterbatch was prepared, and in the second step the masterbatch was mixed with neat-LDPE to obtain a final clay loading of 1-7% (w/w). These films were prepared using LDPE batch MKBX4360V and PE-g-MA batch MKBK3735V.

To prepare the masterbatch, the microcompounder was equipped with extensional flow screws and the mixing barrel was heated to 150 °C. Once the heating blocks were equilibrated, the screw speed was set to speed control mode at 60 rpm with a maximum force tolerance value of 5000 N. 3 g of OMMT and 9 g PE-g-MA were weighed added to the mixing chamber of the micro-compounder using a feed hopper. The screw speed was increased to 120 rpm and the batch mixed for 15 min, after which the screw speed was reduced to 10 rpm and the valve was opened to the exit channel. The melt, which extruded as a strand, was collected and cut into small pellets.

To prepare the OMMT/PE-g-MA/LDPE film, the cast film extrusion die was first attached to the exit channel of the microcompounder. Both the microcompounder and the die were heated to 150 °C and the screw speed was set to 60 rpm. For a certain final OMMT content, 1:3 (w/w) OMMT/PE-g-MA masterbatch and neat LDPE pellets were added to the mixing chamber in proportion listed in **Table S1**. The contents were mixed at 120 rpm for 12-15 min, after which the screw speed control was set to force control mode with a force setting of 550 N, and a maximum speed setting of 120 rpm. The speed (rpm) controlled and torque controlled calendaring rollers were set to values of 450 rpm and 27 N·m, respectively. The polymer melt exiting the film die was grabbed with tweezers and guided on to the rollers for spooling. The polymer melt exiting the film die was cooled with an air-knife set to a flow rate of 35 L min⁻¹. Film thickness was measured by a digital micrometer (Mitutoyo) to typically be in the range of 60-100 micron.

2.8 wt % Arquad 2HT-75 and 21 wt.% PE-g-MA in LDPE. This material was manufactured using a single stage process identical to the second stage of the procedure for fabrication of OMMT/PE-g-MA/LDPE, except during the film extrusion, the torque-controlled roller was set to a value of 30 N·m. The single stage melt was prepared from 2.88 g PE-g-MA, 9.9749 g LDPE, and 0.3683 g Arquad 2HT-75. Note that Arquad 2HT-75 is a hygroscopic solid that becomes sticky when kept under ambient atmosphere; standard practice was to store it in a desiccator and/or pump on it in a vacuum oven overnight prior to weighing it for film incorporation. This film was prepared using LDPE batch MKCB9440 and PE-g-MA batch MKBV7760V.

21 wt % PE-g-MA in LDPE. This material was manufactured using a single stage process identical to the second stage of the procedure for fabrication of OMMT/PE-g-MA/LDPE, except during the film extrusion, the torque-controlled roller was set to a value of 30 N·m. The single-stage melt incorporated 2.808 g PE-g-MA and 10.28 g neat LDPE to afford approximately 21 wt.% PE-g-MA. This film was prepared using LDPE batch MKCB9440 and PE-g-MA batch MKBV7760V.

B. Polymer film characterization

Thermogravimetric analysis (TGA). To determine the total OMMT weight percentage in each CPN cast film, as well as inorganic (MMT) and organic (QAC) fractions, 15-20 mg of the CPN film was sectioned using a hole punch and heated on a platinum pan from ambient temperature to 800 °C with a heating rate

of 20 °C/min on a Q500 TGA (TA Instruments). Tests were performed under nitrogen unless otherwise specified. The inorganic MMT mass fraction in each CPN film was determined by residue analysis (mass residue @ 800 °C / initial mass). To account for any inorganic content originating from the host polymer, the residue % from measurements on neat LDPE films was subtracted from the residue % recorded for the PNCs. The total OMMT weight percentage was determined by scaling the residue % in the PNC by the inorganic fraction of pure Cloisite 20 to account for the weight of organic surfactant that is also lost during the heating cycle. The inorganic fraction of Cloisite 20 was determined to be 61.32 (0.41) % (**Table S3**) by measuring the residual mass after heating a pure sample of Cloisite 20 to 800 °C and accounting for any water weight loss at 100 °C. The QAC content in the CPN film was determined by assuming the MMT:QAC ratio was identical in both the CPNs and in pure Cloisite 20. All samples were measured in triplicate.

Melting point determination. Melting points of OMMT/PE-g-MA/LDPE, Arquad 2HT-75/PE-g-MA/LDPE, and PE-g-MA/LDPE were determined on a Q2000 differential scanning calorimeter (DSC, TA Instruments). Film samples (5-7 mg) were weighed and crimp sealed in 40 μ L Tzero aluminum pans. The temperature scan program used was heat-cool-heat, from – 25 °C to 150 °C, down to 0 °C, then back to 150 °C again, with heating and cooling rates of 10 °C/min and 5 °C/min, respectively. Melting points were calculated using the TA Instruments Universal Analysis software. The melting point was taken as the temperature at which the heating endotherm that dominates the heating cycle reaches its largest magnitude.

FTIR-ATR spectra were acquired on a Perkin Elmer Frontier model FTIR/NIR Spectrometer with an attenuated total reflectance (ATR) accessory featuring a diamond/ZnSe ATR crystal. Typically, polymer films were secured to the ATR film surface using a lever arm that has a force gauge setting that can be used to normalize the pressure applied across samples. During experiments, it was found that spectra of OMMT powder and OMMT/LDPE films were very sensitive to the pressure applied to ensure good contact between the films and the ATR crystal. Unless otherwise indicated, the spectra were therefore recorded with minimal force by tightening the force gauge just until a nonzero reading was indicated in the instrument software. Spectra were reported as the average of 128 independent scans.

X-ray Diffractometry (XRD) was performed on a Brüker D2 Phaser using a copper anode as X-ray source. In a low angle (2 theta $< 10^{\circ}$) configuration to determine OMMT interlayer spacing, an 0.5 mm air scattering screen, 0.1 mm divergence slit, and 3 mm fixed (detector) slit were used to minimize air scatter. The position sensitive detector (PSD) opening was set to half of the initially measured scattering angle (e.g., 0.25° for an initial measured angle of 0.5° 2 theta). In a high angle (2 theta > 10°) configuration, a 2 mm air scattering screen, 1 mm divergence slit, and 8 mm detector slit were used. Film samples were prepared by cutting a 40 mm circular section of film, placing it over a 1 mm thick low background silicon wafer (MTI Corporation), and inserting it into a rear mounted sample holder. All samples were rotated at 15 RPM during measurement. % crystallinity was determined from the high angle data by comparing the fraction of X-rays scattered by LDPE crystalline regions compared to those scattered by the amorphous regions.¹ XRD scattering data over a $10^{\circ} < 2$ theta $< 40^{\circ}$ range was first baselined with a curvature setting of zero using the Diffrac.EVA software provided by Brüker. The baselined data were then separated into amorphous and crystalline regions using peak fitting software (Origin Pro 2017). Both crystalline and amorphous regions were fit to Voigt line shape profiles. For neat LDPE and 1% OMMT/LDPE samples, the amorphous background could be reasonably well fit to single Voigt line shape functions. However, when the wt % of OMMT was > 1%, a single Voigt profile was insufficient to fit the amorphous background, so two peaks were used. Although additional weak crystalline peaks could be detected, for the % crystallinity analysis only the (110) and (200) crystalline Bragg reflections were considered. The % crystallinity was determined from the fitted peak areas by

$$%C = \frac{A_{110} + A_{200}}{A_{110} + A_{200} + A_{amorph}}$$

where A_{110} and A_{200} are the respective areas for the Voigt line shape profiles fitted to the (110) and (200) Bragg reflections, and A_{amorph} is the area of the fitted amorphous background peak (or total area of both peaks for films with OMMT content > 1%).

Scanning Transmission Electron Microscopy. Ultrathin sections of 200 nm or 400 nm nominal thickness were obtained from CPN or neat LDPE samples with a diamond knife (Diatome, Biel, Switzerland) using an ultramicrotome equipped with a cryo chamber (UC7/FC7, Leica, Vienna, Austria) at -140° C. The sections were placed on gold slot grids with a carbon-coated Formvar support film (# FCF2010-Au, Electron Microscopy Sciences, Hatfield, PA, USA) and observed unstained. The prepared sections were analyzed with a dual EDS (Energy Dispersive X-ray Spectroscopy) system (Thermo Fisher Scientific, Madison, WI, USA) in a STEM (Scanning Transmission Electron Microscope) HD2300A (Hitachi, Tokyo, Japan) at 200 kV acceleration voltage, using a 75 μ m objective aperture and 691 pA probe current. Areas were analyzed in "Point and shoot" mode with 120 s live time per area, and for elemental maps 50 to 100 frames were recorded with a dwell time of 400 μ s per pixel per frame.

C. Analysis of QAC concentrations in food simulants

Food simulants were analyzed by flow-injection mass spectrometry (FI/MS). A detailed description of this analysis method is the subject of an earlier publication.² Here we describe basic sample preparation procedure and instrument parameters. All concentrations are expressed on a v/v basis.

Sample preparation. For analysis of 100% ethanol, a 200 μ L aliquot of the sample solution and 50 μ L of a 500 ppb benzyldimethylhexadecylammonium chloride (BDMHD) internal standard solution were added to a 300 μ L vial insert placed in an auto-sampler vial, capped, and briefly vortexed. Aqueous simulants (water, 10% ethanol in water, or 3% aqueous acetic acid) were analyzed by pipetting 200 μ L of the sample solution and 500 μ L ethanol into a 1.7 mL poly(propylene) microcentrifuge tube. After capping, shaking, and briefly vortexing, the contents of the vials were evaporated to dryness in a Turbo-Vap LV at a bath temperature of 50 °C and under a ramped nitrogen pressure ranging from 2-10 psi over a period of ~ 20 min. An additional 100 μ L ethanol was then added to the tube, followed by another round of evaporation. 200 μ L of ethanol containing 100 ppb BDMHD were added to the dried residue in the microcentrifuge tubes, and the tubes were vortexed for approximately 20 seconds. The sample solution was transferred to a 300 μ L glass autosampler vial insert placed in an autosampler vial for analysis.

Quality control (QC) samples were analyzed with most sample sets. These were 100 mL volumes of the food simulant solvent spiked with 1000 ppb (m/v) of Arquad 2HT-75. The QC samples account for analyte stability during the course of the kinetic study and also to monitor adsorption of QACs to sample container walls. In the case of aqueous simulants, it was discovered that QACs in the QC samples were adsorbing onto glass vials; after rinsing QC vials with 100% ethanol and analyzing the rinses, good recoveries were usually achieved (See **Table S8**). A rinsing procedure was therefore also used for the aqueous migration samples to confirm that the low observed migration levels in these samples was not due to QAC adsorption on the sample containers.

Instrumentation. Samples were analyzed by FI/MS on an Acquity-TQD system from Waters Corp (Milford, MA) with a sample manager, solvent manager, degasser, and triple quadrupole mass spectrometer. The Acquity column inlet was plumbed to an Acquity-Guard inline filter, 2.1 mm diameter, 0.2 μ m. No column was used. The mobile phase was 90/10 (v/v) acetonitrile/5 mM aqueous ammonium acetate buffer (pH 5.1). The flow rate was 100 μ L/min. The weak needle wash

solvent was 600 μ L of a 50/50 (v/v) water/isopropanol. The strong needle wash solvent was 1000 μ L of 100% isopropanol. The injection volume was 2 μ L into a 10 μ L loop using partial loop with needle overfill (PLUNO) mode. The total run time was 2 min. The TQD mass spectrometer was run with an electro-spray source in positive mode. The source conditions were: capillary voltage, 1.5 kV; cone voltage, 76 V; extractor voltage, 3 V; radio frequency (RF) voltage, 0.1 V; source temperature, 150 °C; desolvation temperature, 375 °C; cone gas flow, 50 L/hr; desolvation flow, 700 L/hr. The analyzer conditions were set for MS mode with collision gas turned off. Ions were detected in single ion recording (SIR) mode with dwell time of 0.061 s for each target m/z value.

Instrument calibration and sample analysis. Prior to each FI/MS analytical set, the system was cleaned by running at least 8 injections of 50/50 (v/v) isopropanol/dimethylsulfoxide (IPA/DMSO). Two injections of each calibration standard were usually made throughout an analytical sequence. A blank injection of 50/50 IPA/DMSO was made after each standard or sample injection. Analytical sets had more 'flush blanks' than actual standards or samples, which minimizes surfactant ion carry-over. Samples with responses that exceeded the response of the 500 ppb (m/v) calibration standard were diluted with 100 ppb (m/v) BDMHD in ethanol and reinjected. The calibration equation was fit to the standard responses using a quadratic function with 1/x weighting. For samples prepared with the ethanol method (no evaporation step), the surfactant concentrations determined by FI/MS analysis were corrected by a factor of 250/200 to account for the addition of internal standard to the sample. Dilution factors were applied as necessary to account for dilutions needed to keep intensities within the calibration range.

D. Additional discussion of FTIR-ATR spectra of OMMT/LDPE films

During characterization of Cloisite 20/LDPE materials, FTIR-ATR was employed to provide additional information about the dispersion characteristics of the Cloisite 20 platelets. Because the evanescent field extends at most a few microns away from the ATR crystal surface, obtaining good quality spectra is usually contingent on close contact between the ATR crystal and the sample. For solid samples like polymer films, most instruments have a pressure control device that applies downward pressure to maintain good contact between the sample and the crystal. Typically, increasing the vertical pressure will increase the intensity of vibrational bands by bringing more oscillators into the evanescent field, and for many rigid samples the frequency and relative intensity of vibrational peaks will not undergo significant shifting unless the chemical and physical nature of oscillators change during compression.

During measurement of OMMT/LDPE films and neat MMT powders, it was discovered that the position and intensity of the various in-plane and out-of-plane peaks in the Si-O stretching region were highly sensitive to the pressure reading on the ATR force gauge. Although the spectral intensity of all peaks was expected to increase as the pressure gauge was increased, some peaks intensified out of proportion to other peaks and also shifted position, signaling that the application of pressure to the sample was changing the physical nature of Si-O stretches in the MMT clays.

Figure S2 displays FTIR-ATR spectra for (a) 1 wt%, (b) 3 wt%, (c) 5 wt%, and (d) 7 wt%, as well as (e) neat Cloisite 20 and (f) neat Cloisite 116 powders recorded at three force gauge readings: 0, 5, and 30. Additional force values were explored, but for LDPE-containing samples, no further spectral changes were observed after the force gauge reading was increased beyond a value of 30. Powders continued to manifest changes up to a force setting of 80. (Note, we have inquired with the manufacturer about whether the force gauge reading is associated with a specific force or pressure unit, and it was indicated that the value is provided only to ensure a similar force

across samples, so we do not provide a specific unit for the force reading here.) Note that because compression of the films brings more OMMT platelets within the penetration depth of the evanescent field, all peaks in the Si-O stretching region spectral envelope increase in intensity as the force gauge reading is increased. Therefore, the spectra in **Figure S2** have been normalized to the Peak III intensity (at about 1040 cm⁻¹) to facilitate changes in the different peak intensities relative to each other.

The results shown in Figure S2 support the conclusion that OMMT platelets dispersed in LDPE are partially aligned parallel to the film plane, probably as a result of torque applied during the drawing of the melt through the film die. When the Cloisite 20 concentration in LDPE was low (e.g., 1%, Figure S2a), increasing the force gauge setting resulted in almost no change to the Peak III/IV envelope shape but significant intensification, with no shift, of Peak II. Because the ATR experiment is inherently polarized due to a larger effective path length for incident light polarized parallel to the plane of incidence,³ particularly at frequencies below 1500 cm⁻¹, enhancement of Peak II at about 1080 cm⁻¹ were taken as evidence that a high proportion of the out-of-plane stretching vibrations are brought into better alignment with the plane of incidence (perpendicular to the experimental plane) as pressure is brought to bear on the sample. (The absorptivity of any given oscillator is a function of the dot product of the light polarization vector and the vector of the dipole moment change associated with the vibration; as the mean angle between the out-ofplane Si-O stretching vibration and the fixed light polarization vector decreases, the intensity of the Si-O stretching vibration increases, even if the concentration of oscillators is fixed.) As the force gauge reading is increased, we speculate that the average degree of alignment between OMMTs and the film film/crystal plane would improve only if the platelets already possessed some degree of preferred alignment parallel to the film direction, because the force is applied perpendicular to the film/crystal plane. Note that increasing the force gauge reading does not change the Peak II vibrational frequency, meaning that application of force does not appreciably change the interplatelet distance, at least over the range at which the out-of-plane Si-O vibration is sensitive to such changes. Similar effects are seen for OMMT/LDPE films with other OMMT weight percentages (Figure S2b-d).

From a methodological standpoint, the sensitivity of the silicon-oxygen stretching vibrations to the force gauge reading highlights the importance of recording FTIR-ATR spectra of CPN materials in zero-force mode to give an accurate accounting of the MMT dispersion characteristics. We note that the effect of compression on the Si-O stretching vibrations are even more severe in OMMT powders, which feature much more compressible interplatelet volume elements (e.g., air). The peak maximum of the Si-O vibration spectral envelope shifts from 1044 cm⁻¹ in the Cloisite 20 spectrum at a force reading of zero all the way to 1005 cm⁻¹ at a force reading of 80.

E. Selection of input parameters for migration modelling using Fick's Second Law

As mentioned in the text, the amount of QAC migrating from the CPN film into the surrounding food simulant at time t (M_{F,t}) can be determined from these two parameters using Fick's second law, which has the following analytical solution for diffusion from a polymer⁴⁻⁵:

(1)
$$\frac{M_{F,t}}{A} = c_{P,0}\rho_P d_P \left(\frac{\alpha}{1+\alpha}\right) \left[1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp\left(-D_P t \frac{q_n^2}{d_P^2}\right)\right]$$

where $\alpha = \frac{1}{K_{P,F}} \frac{V_F}{V_P}$, $K_{P,F} = \frac{c_{P,\infty}}{c_{F,\infty}} \frac{\rho_P}{\rho_F}$, and $\tan q_n = -\alpha q_n$

Definitions of the input parameters and how they were determined:

A is the total contact area in cm². Test samples were 42 mm diameter circles, giving a onesided surface area of 13.85 cm². Because migration can happen from either side of the film, a total contact area of 27.71 cm² was used. The film thickness, d_P (cm), was taken as half the actual thickness because QACs can migrate to either side of the film. Each replicate film had a different thickness, so $M_{F,t}$ calculations were performed in triplicate and averaged.

 $c_{P,\theta}$ is the concentration (µg g⁻¹) of QAC in the polymer before the migration experiment. The initial concentration of C18-C18 QACs in the CPN was determined by starting the initial total QAC content in the film: 2.705 wt % (**Table S3D**; this was a Series II film). The C18-C18 QACs have a relative abundance in our lot of Arquad 2HT-75 of 36.48 % (**Table 2**), so $c_{P,0} = 0.987$ wt %, or 9870 µg g⁻¹. However, only 4-10% of the QACs in Cloisite 20 are recoverable via extraction experiments on CPNs. We have taken 10% as an upper limit of the effective portion of QACs in CPNs that are available for migration. Therefore, we have estimated $c_{P,0} = 987$ µg g⁻¹.

The partition coefficient, $K_{P,F}$, of QACs was determined from the migration data for the film containing 4 wt % Arquad 2HT-75 in LDPE, and was assumed to be identical to the $K_{P,F}$ value for the Cloisite 20 film (e.g., the clay platelets minimal influence over the solubility of the "available" QACs in the polymer phase). The partition coefficient is usually determined by measuring the relative concentration of the additive in the polymer and simulant phases at equilibrium ("infinite time"). For the Arquad 2HT-75 migration experiment, we have taken 696 hours to approximate "infinite time" because there was no observed increase in the migration between 485 and 696 hours. The mean concentration of QACs in the simulant was determined experimentally to be 8697.2 µg mL⁻¹ at 696 hours. Based on this value and the known initial QAC content in this material (3.15 wt % of QACs in the 4 wt % Arquad 2HT-75 film x 36.85 wt % C18-C18 abundance = 1.147 wt % C18-C18 QACs in the 4 wt % Arquad 2HT-75 film = 11470 µg g⁻¹), a mean value of $c_{P,\infty}$ was determined to be 1934.8 µg g⁻¹. Using an estimated polymer density of 0.925 g mL⁻¹ and an ethanol density of 0.772 g mL⁻¹ at 40 °C, $K_{P,F}$ was determined to be ~205 as an average across three replicates. This may be a slight overestimate of the partition coefficient because migration was assumed to be complete at 696 hours.

α: Based on the $K_{P,F}$ value of 205 and mean volumes of the test films and simulants (100 mL), α was determined to be equal to 5.05.

 q_n values were determined by finding the positive roots to the equation $tan(q_n) + \alpha q_n = 0$. Although the summation in equation (1) is over an infinite number of terms, the equation was truncated at 14 terms.

Supplemental Figures



Figure S1. Thermogravimetric analysis of Cloisite 20 powder. Ramp speed was 20 °C/min. Test was performed under N_2 gas until 600 °C, at which point the purge gas was switched to air.



Figure S2. FTIR-ATR spectra of (a) 1 wt%, (b) 3 wt%, (c) 5 wt%, and (d) 7 wt% OMMT in PE-g-MA/LDPE, as well as (e) neat Cloisite 20 and (f) neat Cloisite 116 powder, at three different force gauge settings. Higher force gauge value equals more film compression. Each spectrum is the average of 128 scans and has been normalized to the Peak III intensity (at around 1040 cm⁻¹). The films used for this figure were from Series I.



Figure S3. Representative X-ray diffractograms of neat LDPE and OMMT/PE-g-MA/LDPE films with OMMT content ranging from 1-7 wt% recorded from 10-35° 20 for crystallinity determination. The spectra are offset for clarity and were corrected by subtracting a background using the DIFFRAC.EVA instrument software with a curvature setting of 0. The 110 and 200 LDPE crystalline Bragg reflections are indicated. The films were from Series I.



Figure S4. Plots of crystallinity (left) and the peak area ratio of the 110 and 200 Bragg reflections (right) as determined by XRD for neat LDPE and OMMT/PE-g-MA/LDPE films with OMMT content ranging from 1-7 wt %. The plotted values are the means over three replicates and the error bars represent standard deviations.



Figure S5. Representative mass spectrum in positive ionization mode of 100% ethanol stored in the presence of (A) neat LDPE or (B) 7 wt % OMMT/PE-g-MA/LDPE film at 75 °C for 30 days. The insets show expanded views of the 460-560 m/z range for each experiment. Selected QACs in the Arquad 2HT-75 mixture are indicated by asterisks, and these peaks are also labelled with their corresponding m/z values in the panel (B) inset. Peaks that show up in both panel A and panel B, generally outside the m/z = 460-560 region, correspond to compounds incorporated into the polymer by the manufacturer (see **Table S4**).



Figure S6. Experimental migration data (black squares) for QACs with m/z = 550.6 (C18-C18) from a 4% Arquad 2HT-75/PE-g-MA/LDPE film along with data simulated from an analytical solution to Fick's Second Law (Eqn. 1) based on a D_P value of 4.0 x 10^{-12} cm² s⁻¹. This value was determined by a least squares fit to the experimental fit to the data. Each experimental data point is the mean of three independent replicates and the error bars represent standard deviations.



Figure S7. Total mass of QACs migrated from a OMMT/PE-g-MA/LDPE film with nominal Cloisite 20 content of 5 wt % after storage for 10 days at 25 °C, 40 °C, or 66 °C. The mass ratio of Cloisite 20 to PE-g-MA was 1:3. The total QAC migration is the sum of QACs having molecular weights of 550.6, 522.6, 494.6 and 466.5 g mol⁻¹, divided by the initial film mass. The red and blue lines represent data acquired from experiments using two completely different sets of PNC films, which have been called Series I and Series II. Error bars represent the standard deviation from the mean migrated total QAC mass (n = 3).

Supplemental Tables

Final OMMT wt.%	Mass [g] of 1:3 (w/w) OMMT/PE-g-MA added	Mass [g] of neat LDPE resin added
1	0.48	11.52
3	1.44	10.56
5	2.40	9.60
7	3.36	8.64

 Table S1. Masses of 1:3 (w/w) OMMT/PE-g-MA masterbatch and neat LDPE resin used to manufacture OMMT/PE-g-MA/LDPE CPNs with varying final wt.% of OMMT

Film ID	OMMT ^a			Arquad	PE-g-	LDPE
	Total	MMT	QACs	2HT-75 ^b	MA	
	(inorganic	(inorganic)	(organic)			
	+ organic)					
Neat LDPE	0	0	0	0	0	100
1% OMMT/LDPE	1	0.61	0.39	0	3	96
3% OMMT/LDPE	3	1.83	1.17	0	9	88
5% OMMT/LDPE	5	3.05	1.95	0	15	80
7% OMMT/LDPE	7	4.27	2.73	0	21	72
Neat LDPE w/ PE-	0	0	0	0	21	79
g-MA						
Arquad 2HT-75/	0	0	0	4.00/3.15	21	75
LDPE						

Table S2. Nominal composition (in wt%) of CPN and control films made in this study

^aBy thermogravimetric analysis, the composition of Cloisite 20 OMMT lot# 5102006 was found to be 61.3% inorganic clay by weight, the remainder being organic QACs originating from Arquad 2HT-75. See **Figure S1**. ^bThe Arquad 2HT-75 lot we employed constituted about 70% by weight the four major QAC targets. Based on the abundance of all QACs in the sample (See main text, Table 2), the Arquad 2HT-75 is estimated to be 78.8% QACs by weight. By adding 4 wt% Arquad 2HT-75, this results in a final theoretical QAC concentration (3.15 wt %), close to that in the 7 wt % OMMT/LDPE film (2.73 wt %). Because Arquad 2HT-75 is a sticky solid, there is potential for slightly less than 100% incorporation of the weighed quantity into the melt. This was our justification for adding Arquad 2HT-75 in slight excess during manufacture of the positive control Arquad 2HT-75/LDPE film, so that the final QAC concentration of QACs in the Arquad 2HT-75/LDPE and 7 wt % OMMT/LDPE films would be reasonably close. **Table S3.** Thermogravimetric data^a for clay containing materials and some control materials

A. Cloisite 20	(OMMT) powder	
Material	Residual (inorganic)	Calculated initial
	mass at 800 $^{\circ}C^{b}$	organic content ^c
	[wt%]	[wt%]
Cloisite 20	61.317 (0.409)	38.683 (0.409)

B. Neat LDPE Film

Material	Residual (inorganic) mass at 800 °C ^b [wt%]	Calculated initial organic content ^c [wt%]
LDPE film	0.221 (0.045)	99.779 (0.045)

C. OMMT/PE-g-MA/LDPE film. Series I

Nominal	Residual (inorganic)	Calculated initial	Calculated initial
OMMT weight	mass at 800 °C ^b	OMMT content ^{<i>a</i>}	QAC content ^{<i>e</i>}
content	[wt%]	[wt%]	[wt%]
1%	0.778 (0.129)	1.268 (0.211)	0.491 (0.082)
3%	1.991 (0.072)	3.247 (0.120)	1.256 (0.049)
5%	3.180 (0.073)	5.187 (0.124)	2.006 (0.054)
7%	4.497 (0.073)	7.334 (0.128)	2.837(0.061)

D. OMMT/PE-g-MA/LDPE film, Series II

Nominal	Residual (inorganic)	Calculated initial	Calculated initial
OMMT weight	mass at 800 °C ^b	OMMT content ^{<i>d</i>}	QAC content ^{<i>e</i>}
content	[wt%]	[wt%]	[wt%]
1%	0.695 (0.204)	1.134 (0.332)	0.439 (0.129)
3%	1.803 (0.152)	2.941 (0.248)	1.137 (0.097)
5%	3.096 (0.050)	5.050 (0.088)	1.953 (0.042)
7%	4.288 (0.076)	6.994 (0.132)	2.705 (0.061)

^aAll data reported are mean values for 3 independent replicates. Numbers in parentheses for measured residual weight values are standard deviations. For calculated values, propagated errors based on the standard deviations are reported. ^bThe values are based on the "dry weight" of the clay. To account for the small amount of water content in the Cloisite 20 powder (see Figure S1), the starting clay weight in each replicate was determined by scaling the initial clay weight by the residual weight measured at 100 °C. The mean weight loss at 100 °C over the three replicates was 0.59 (0.04) wt%, indicating that this constitutes a small correction to the residue analysis. There was no observable change in weight for LDPE or OMMT/LDPE films between 25 and 100 °C. indicating negligible water content. Therefore, this correction was not performed for these materials. ^cAssuming that the residual mass (X) at 800 °C is exclusively inorganic material, the initial organic (QAC) fraction of Cloisite 20 was determined as 100-X. ^dThe initial OMMT content in CPN films was determined by dividing the residual inorganic weight % at 800 °C by the residual weight fraction of neat OMMT (Cloisite 20) powder at 800 °C. "The initial QAC content was determined by taking the difference of the calculated initial OMMT content (which consists of inorganic MMT clay and QAC surfactant) and the residual measured inorganic weight at 800 °C (which consists only of inorganic MMT clay).

ID	Function	Ion	Formula	Calc. m/z	Exptl. m/z
Glycerol	Lubricant	$[M+H-H_2O]^+$	C19H37O3	313.274	313.273
monopalmitate					
Glycerol	Lubricant	$[M+H]^+$	C19H39O4	331.285	331.283
monopalmitate					
Erucamide (13-	Slip agent /	$[M+H]^+$	C ₂₂ H ₄₄ NO	338.342	338.342
docosenaide)	antiblocking				
Glycerol	Lubricant	$[M+H-H_2O]^+$	$C_{21}H_{41}O_3$	341.305	341.304
monostearate					
Glycerol	Lubricant	$[M+H]^+$	$C_{21}H_{43}O_4$	359.316	359.346
monostearate					
4-ethylbenzyl-	Clarifying /	$[M+H]^+$	$C_{24}H_{31}O_6$	415.212	415.211
idene sorbitol	nucleating				
	agent				
4-ethylbenzyl-	Clarifying /	$[M+Na]^+$	C24H30O6Na	437.194	437.193
idene sorbitol	nucleating				
	agent				
Diglyceride	Lubricant	$[M+H-H_2O]^+$	C37H71O4	579.533	579.535
34:0					
Diglyceride	Lubricant	$[M+H-H_2O]^+$	C39H75O4	607.566	607.566
36:0					
Irgafos 168	Antioxidant	$[M+H]^{+}$	C42H64O3P	647.459	647.459
Irgafos 168	Antioxidant	$[M+H]^{+}$	$C_{42}H_{64}O_4P$	663.448	663.454
(oxidized)					
Irgafos 168	Antioxidant	$[M+Na]^+$	C42H63O4PNa	685.436	685.436
(oxidized)					

Table S4. List of additives identified in the LDPE resin that migrated to ethanol based on the MS spectrum shown in Figure $5.^{a}$

^{*a*}In addition to the positively identified peaks listed here, a large group of peaks is observed in the m/z = 540 to 610 region. Although the precise chemical species responsible for these peaks has not been identified, based on carbon isotopic peak separations and pattern similarities relative to the assigned (stearate and palmitate based) diacylglyceride species at m/z = 579.533 and m/z = 607.564, it is believed these peaks are due to fragmentation of divalent dimer cations of these diacylglycerides, which serve a lubricant function in the LDPE resin. The spectral data were obtained on an Exactive orbitrap high-resolution mass spectrometer.

	Time	MW =	550.6	MW =	522.6	MW =	494.6	MW =	466.5	Tot	tal
	[hr]	[µg	/g]	[µg	/g]	[µg	/g]	[µg	/g]	[µg	/g]
		Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD
	2	37.15	3.03	41.54	3.99	17.11	1.73	< 6.48		<102.27	
	4	47.51	2.18	53.50	2.74	21.97	1.02	< 6.48		<129.46	
	8	71.63	5.94	80.71	7.03	32.84	2.93	< 6.48		<191.65	
0 V	12	78.23	4.64	87.35	5.21	35.70	2.20	<6.48		<207.75	
PH e 2	24	107.80	7.94	120.18	9.59	48.61	3.69	9.35	0.72	285.94	21.90
CD - B-	48	153.93	12.43	172.54	13.39	69.14	4.62	13.22	0.72	408.83	31.15
PE %]	72	189.31	26.70	211.82	27.39	83.84	9.41	16.06	1.68	501.03	65.16
6 C	96	206.25	12.64	232.08	12.32	92.56	4.24	17.68	0.80	548.57	29.77
219	168	347.37	20.88	385.34	23.07	148.06	7.55	27.14	1.41	907.91	52.87
	240	371.80	34.33	425.10	36.63	162.12	12.21	29.40	2.26	998.43	85.36
	485	594.80	17.97	682.58	19.72	270.46	8.90	31.40	2.22	1579.24	47.17
	696	683.08	35.01	777.80	41.22	311.87	17.52	47.74	9.44	1820.49	103.16
	2	649.44	176.08	698.01	187.09	215.57	49.29	37.37	7.90	1600.39	420.18
1%	4	732.85	164.99	795.86	177.68	240.18	47.79	41.64	7.87	1810.54	398.27
12	8	771.55	183.44	848.33	207.09	256.80	51.96	44.82	8.69	1921.49	451.04
1 2 – EJ	12	1028.69	422.42	1185.93	540.72	302.89	81.46	52.04	12.73	2569.55	1055.01
T A	24	916.51	138.01	989.87	142.99	359.18	49.60	66.20	8.97	2331.76	339.50
H V- C	48	1227.13	165.10	1323.65	172.87	480.15	57.98	88.25	10.22	3119.18	406.09
d d d	72	1707.71	245.23	1827.56	248.66	647.72	80.81	117.27	13.58	4300.26	588.16
na 75°	96	2307.90	226.52	2464.71	235.67	854.58	73.22	153.33	12.52	5780.53	547.75
bu	168	5639.99	423.58	5944.25	437.93	2020.51	149.32	344.48	23.62	13949.24	1033.86
V O	240	7517.09	309.52	7944.65	385.59	2626.71	159.12	447.57	28.68	18536.01	880.62
4	485	10079.41	1223.97	10816.24	1313.23	3732.53	453.89	603.13	73.22	25231.31	3064.19
	696	9535.07	350.25	10228.97	323.07	3514.15	117.88	596.50	15.17	23874.69	805.57
	2	< 4.94		< 4.94		< 4.94		< 4.94		<19.75	
~	4	< 4.94		< 4.94		< 4.94		< 4.94		<19.75	
T 🖂	8	< 4.94		< 4.94		< 4.94		< 4.94		<19.75	
N- Id	12	< 4.94		< 4.94		< 4.94		< 4.94		<19.75	
E-g	24	< 4.94		< 4.94		< 4.94		< 4.94		<19.75	
PE %	48	< 4.94		< 4.94		< 4.94		< 4.94		<19.75	
%	72	< 4.94		< 4.94		< 4.94		< 4.94		<19.75	
51	96	< 4.94		< 4.94		< 4.94		< 4.94		<19.75	
	168	< 4.94		< 4.94		< 4.94		< 4.94		<19.75	
	240	< 4.94		< 4.94		< 4.94		< 4.94		<19.75	

Table S5. Migration of four target QACs from OMMT/PE-g-MA/LDPE, Arquad 2HT-75/PA-g-MA/LDPE, and PE-g-MA/LDPE into 100% ethanol as a function of time at 40 °C^{*a*}

"The reported values are the masses (in μ g) of the respective QACs transferred to each food simulant per g film mass, as measured by flow-injection mass spectrometry. The means and standard deviations were determined in each case across three independent replicates. Samples with reported values after a less than "<" symbol had at least one replicate with a concentration below the LOQ. The reported value was determined by assuming the concentration in these replicates was equal to the LOQ value and then calculating the mean across the replicates; an upper limit to the migration is implied by this result.

Table S6 Migration of QACs from OMMT/PA-g-MA/LDPE with different OMMT mass loadings into 100% ethanol after storage for 10 days at 40 $^{\circ}C^{a}$

Α.	Series I	

Mass %	MW = 550.6	MW = 522.6	MW = 494.6	MW = 466.5	Total
OMMT ^b	[µg/g]	[µg/g]	[µg/g]	[µg/g]	[µg/g]
0	< 2.99	< 3.57	< 2.99	< 2.99	< 12.54
1	37.09 (2.37)	39.18 (2.21)	14.82 (0.70)	2.32 (0.10)	93.41 (5.37)
3	55.19 (1.06)	58.66 (1.20)	22.87 (0.72)	4.16 (0.24)	140.88 (3.11)
5	161.04 (7.41)	166.32 (7.94)	62.62 (3.11)	11.09 (0.57)	401.63 (18.84)
7	207.32 (12.59)	213.25 (13.23)	82.16 (5.56)	14.58 (1.11)	517.32 (32.49)

B. Series II

Mass %	MW=550.6	MW=522.6	MW=494.6	MW=466.5	Total
OMMT ^b	[µg/g]	[µg/g]	[µg/cm ²]	[µg/g]	[µg/g]
0	< 3.49	< 3.49	< 3.49	< 3.49	< 13.95
1	29.92 (8.12)	33.09 (8.83)	13.47 (3.60)	< 3.86	< 80.35
3	61.90 (4.59)	67.27 (4.92)	28.12 (2.21)	5.64 (0.48)	162.93 (12.19)
5	182.47 (10.73)	196.88 (83.64)	83.64 (4.91)	17.30 (1.04)	480.29 (28.17)
7	222.06 (19.56)	249.62 (24.19)	110.74 (10.48)	23.91 (2.19)	606.33 (56.36)

^{*a*}The reported values are the mean mass of the respective QACs transferred to the food simulant per unit film mass, as measured by flow-injection mass spectrometry. The values in parentheses represent standard deviations of three independent replicates. The LOQ for the analytical method in solution was 5 ppb, which determines the LOQ on a per-film-mass basis. Samples with reported values after a less than "<" symbol had at least one replicate with a concentration below the LOQ. The reported value was determined by assuming the concentration in these replicates to be equal to the LOQ value and then calculating the mean; an upper limit to the migration is implied by this result. ^{*b*}The values reported here are the nominal mass % of Cloisite 20 in the materials. The actual mass % values of Cloisite 20 in the 1, 3, 5, and 7 mass % films are provided in **Table S3**.

Table S7. Migration of QACs from Cloisite 20/PE-g-MA/LDPE^{*a*} and control film into 100% ethanol as a function of temperature after 10 days^{*b*}

Mass %	Temp.	MW = 550.6	MW = 522.6	MW = 494.6	MW = 466.5	Total
OMMT	[C °]	[µg/g]	[µg/g]	[µg/g]	[µg/g]	[µg/g]
Clay	25	48.33	53.02	20.67	4.25	126.28
film		(8.01)	(8.74)	(3.66)	(0.73)	(21.13)
(5 wt %)	40	161.04	166.32	62.62	11.09	401.06
		(7.41)	(7.94)	(3.11)	(0.57)	(18.84)
	66	625.02	641.46	233.63	34.83	1534.94
		(27.09)	(27.77)	(9.70)	(1.06)	(65.59)
Control	25	3.84	< 3.61	< 2.84	< 2.84	< 13.14
Film		(0.34)				
	40	< 2.95	< 3.52	< 2.95	< 2.95	< 12.38
	66 ^c	4.90	4.90	< 3.20	< 3.20	< 16.10
		(0.70)	(0.30)			

A. Series I

B. Series II

Sample	Temp.	MW = 550.6	MW = 522.6	MW = 494.6	MW = 466.5	Total
	[C°]	[µg/g]	[µg/g]	[µg/g]	[µg/g]	[µg/g]
Clay	25	49.24	55.11	23.84	4.92	133.10
film		(9.01)	(9.85)	(4.29)	(0.88)	(24.03)
(5 wt %)	40	182.47	196.88	83.64	17.30	480.29
		(10.73)	(11.52)	(4.91)	(1.04)	(28.17)
	66	817.29	899.04	378.78	58.47	2153.58
		(26.48)	(27.92)	(11.87)	(1.55)	(67.54)
Control	25	< 3.55	< 3.55	< 3.55	< 3.55	< 14.19
film	40	< 3.49	< 3.49	< 3.49	< 3.49	< 13.95
	66	< 3.47	< 3.47	< 3.47	< 3.47	< 13.90

^{*a*}The nominal mass ratio of Cloisite 20 to PA-g-MA to LDPE in this film prior to the migration test was 5:15:80. ^{*b*}The reported values are the mean mass of the respective QACs transferred to the food simulant per unit film mass, as measured by flow-injection mass spectrometry. The values in parentheses represent standard deviations of three independent replicates. Samples with reported values after a less than "<" symbol had at least one replicate with a concentration below the LOQ. The reported value was determined by assuming the concentration in these replicates to be equal to the LOQ value and then calculating the mean across the replicates; an upper limit to the migration is implied by this result. ^{*c*}One replicate in this experiment was contaminated with QACs. Therefore, the reported value is an average of only two replicates.

Table S8. Percent recoveries of QACs from QC samples in 100 mL of food simulants stored for 10 days at 40 °C, in three 20 mL ethanol rinses after decanting of the simulant, and in total of simulants and rinses

QAC	Sample	100% ethanol	100% water	10% ethanol in water	3% acetic acid in water
MW = 550.6	Simulant	91.6	67.4	8.7	64.0
	Rinses	0.5	27.8	85.8	27.8
	Total	92.1	95.3	94.5	91.8
MW = 522.6	Simulant	85.1	43.0	4.7	59.2
	Rinses	0.6	48.1	91.4	31.6
	Total	85.7	91.1	96.2	90.8
MW = 494.6	Simulant	97.5	40.2	2.3	57.3
	Rinses	0.0	54.6	98.6	33.5
	Total	97.5	94.8	100.9	90.8
MW = 466.5	Simulant	98.9	36.0	0.0	57.4
	Rinses	0.0	62.8	108.7	30.3
	Total	98.9	98.8	108.7	87.7

References

- 1. Rabiej, S., A comparison of 2 X-ray Diffraction Procedures for Crystallinity Determination. *Eur. Polym. J.* **1991**, *27* (9), 947-954.
- Yu, L.; Malik, S.; Duncan, T. V.; Jablonski, J. E., High Throughput Quantification of Quaternary Ammonium Cations in Food Simulants by Flow-Injection Mass Spectrometry. J. AOAC. Int. 2018, 101, 1873-1880.
- 3. Averett, L. A.; Griffiths, P. R.; Hishikida, K., Effective path length in attenuated total reflection spectroscopy. *Anal. Chem.* **2008**, *80* (8), 3045-3049.
- 4. Begley, T.; Castle, L.; Feigenbaum, A.; Franz, R.; Hinrichs, K.; Lickly, T.; Mercea, P.; Milana, M.; O'Brien, A.; Rebre, S.; Rijk, R.; Piringer, O., Evaluation of migration models that might be used in support of regulations for food-contact plastics. *Food Addit Contam* **2005**, *22* (1), 73-90.
- 5. Brandsch, J.; Mercea, P.; Ruter, M.; Tosa, V.; Piringer, O., Migration modelling as a tool for quality assurance of food packaging. *Food Addit. Contam., Part A* **2002**, *19*, 29-41.