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Minbloc[®]HC

High-Clarity Antiblock Additive for Films

Engineered mineral fillers for polyolefin film applications

Mineral additives are widely used to enhance the performance and value of polyolefin film products. This paper investigates the effects of particle size distribution, refractive index, mineral composition, and particle morphology on a range of properties of interest in packaging and horticultural film applications. These structure/property effects are highlighted using nepheline syenite mineral additives with engineered particle size distributions (PSD). Results demonstrate that control of mineral filler characteristics can be used to optimize a range of end use performance properties of polyolefin films.

Introduction

Mineral additives are used to optimize polyolefin film performance in many ways. Examples include improved processing efficiency, enhanced mechanical properties, modified surface characteristics, and controlled gas transmission rates. This paper focuses on mineral additive usage in two common applications, namely antiblocking in packaging films, and control of light transmission properties in horticultural (greenhouse) films.

An antiblock decreases blocking or "sticking" of films together to improve separation of stacked film; lower blocking values (expressed in grams) are better. Figure 1 shows the typical surface roughening effect in polyolefin film as characterized using Atomic Force Microscopy. The mineral additive (in this case nepheline syenite) increases surface roughness and decreases blocking. Mineral fillers are also used in greenhouse films to control heat loss and optimize crop growth. Performance is expressed as thermicity, which is the fraction of infrared heat radiation that is lost by the greenhouse; lower thermicity values are better. Mineral concentrations are significantly different in these two applications. When used as an antiblock typical addition levels are 1,500-10,000 ppm (with specific loadings depending on polymer type, film thickness, and application); as a thermal film additive loading levels of 3 to 10 wt% are typical.

For more information about MINBLOC plastic film additives, please call: 800.243.9004 or email: Sales@CoviaCorp.com.



Nepheline syenite, manufactured by Covia Holdings LLC as MINEX® Functional Fillers and Extenders, has been used in paints and coatings for nearly forty years. However its widespread use in plastic films, sold under the MINBLOC® HC Plastic Film Additives brand, is relatively new. Chemically, nepheline syenite is classified as anhydrous sodium potassium alumino silicate. Geologically, it is composed of three minerals: soda and potash feldspar, and the mineral nepheline. Nepheline syenite provides the physical properties of hard and inert functional fillers and has the best Health, Safety and Environmental (HS&E) profile as it does not contain free crystalline silica. It has relatively low surface area and is readily dispersible in polymer systems. Performance can be optimized for specific applications using proprietary mineral processing methods used to control particle size distribution.



Table 1 lists the typical properties of nepheline syenite. This mineral has both angular and blocky particles; SEM images of three different grades are shown in Figure 2.

Table 1: Typical properties of nepheline syenite

Particle Shape	Rectangular, angular and nodular
Specific Gravity, g/ml	2.61
Mohs Hardness	6
Brightness (tappi)	85 - 94
Oil Absorption, % (ASTM 281)	22 – 35
Refractive Index	1.51 – 1.53
Moisture, % (ASTM C-566)	0.05 – 0.15
Surface Area m ₂ /g	0.6 – 1.7
Hegman value	3 – 7
pH (20 % Slurry)	9.5 – 10.5



a) Standard

b) Narrow PSD 2

Figure 2: SEM images (2,000X) of three different grades of nepheline syenite representing standard, narrow and ultra-fine particle size distributions.

Table 2: Properties of nepheline syenite grades

Grade	HC 1400	EP 315	Experimental
Median Particle Size, microns	7	9	10
Particle Size between 5 and 15 microns, %	70	80	90
Particle Top-size	15	15	20
Oil Absorption, % (ASTM 281)	27	24	22
Surface Area m²/g	2.4	1.0	0.9



c) Ultra-fine

Refractive index (RI) and particle size distribution (PSD) affect the functionality of the additive. Comparison of RI values of various fillers and resins is made in Figure 3. Discounting interfacial effects (which are also important), transparency is optimized when the RI of the mineral approximates that of the host polymer. The RI of nepheline syenite is in the range of 1.50 to 1.53, which is a close match for polyolefins as well as many other common polymers (Figure 3). A visual example of the obtainable optical clarity with nepheline syenite fillers and antiblocks is provided in Figure 4. The PSD of the filler can be engineered, by controlling the mean and the width of the distribution.



Figure 3: RI Comparison of polyolefins with selected mineral additives. The boxed area denotes the range where nepheline syenite matches polymer refractive index.

Figure 5: Particle size distributions of various engineered NS grades.



Figure 4: Image clarity of 4.0 mil LDPE film filled with standard NS at 0, 5, 10, and 20 wt% loadings.

Experimental

Properties of the different nepheline syenite grades used in this paper are shown in Table 2. PSD differences of selected engineered grades are shown graphically in Figure 5. Samples were prepared with a Brabender TSE 20/ 40 clam-shell twin screw extruder (20 mm, L/D 40, 6 heating zones) driven by an Intelli-Torque Rheometer. Films were prepared with a single screw extruder (19 mm, L/D 25), equipped with a blown film die (1 inch) and blown film take-off tower. Selected film samples used in this study were prepared and analyzed by third party toll compounders and laboratories. The LDPE resin used for all films was Lyondell Basell Petrothene NA345-013 (MFI: 1.8; specific gravity: 0.921). Filler loadings used for antiblock and thermal filler applications were 2,500 ppm and 10% by weight (wt%), respectively, unless otherwise specified. Antiblock films were prepared with 1.25 mil thickness; thermal films were prepared at 4 mil thickness unless otherwise noted. Filler particle size distributions (PSD) were measured with laser diffraction. Properties such as antiblocking, haze (Hazemeter), and color (Colorimeter) were measured according to ASTM methods. Thermicity was measured with Fourier-transform infrared spectroscopy (FTIR). Powder flow was measured with a Brookfield powder flow tester.



Results and discussion

When comparing different fillers in antiblock and thermal film applications, variations in optical properties as a function of the mineral refractive index can be observed. The best optical properties, or lowest haze values, are observed when mineral RI best matches that of the resin. This is illustrated in Figure 6: though absolute haze values are a function of film thickness and mineral concentration, lowest haze occurs when there is a refractive index match of mineral and polymer. Other factors can also affect optical properties as will be discussed below.

An important functional filler property that can be engineered is the PSD. This affects both antiblocking performance and thermal filler efficiency. The PSD is defined not only by the mean diameter of the particle but also by the shape (defined by values such as variance and skew). Dependence of blocking and thermicity on the mean particle size (d50) is shown in Figure 7. The optimal d50 values for antiblocking and thermicity are obtained for nepheline syenite at around 7 and 10 microns, respectively. For thin films, antiblocking depends not only on the filler's d50 value but also on the film thickness. As expected, particularly small particles are not very efficient as an antiblocking agent since performance depends on bumps at the surface of the film formed by the mineral. On the other hand, large particles are not as efficient in very thin films or skin layers, and can also lead to film defects and process equipment abrasion.

Optical properties depend on the particle size as well. The smaller the particle size, the lower the haze in both antiblocking and thermal film applications (Figure 8). A physical phenomenon is causing this effect. Larger particles tend to cause larger bumps at the surface, which physically separate the stacked films to provide antiblocking. These surface bumps also causes light scattering analogous to water droplets on a windowpane,





Figure 6: Best haze values are obtained in antiblocking (top) and thermal film (bottom) applications when the functional filler closely matches the R.I. of the resin (LDPE R.I. = 1.51). Two film thicknesses were studied for thermal film: 4 mil (red square) and 6 mil (blue diamond).

Figure 7: Antiblock (top) and thermal filler (bottom) performance is maximized at an optimal mean particle size. The films with antiblock were blown at different thicknesses. Thermicity data obtained using hot pressed (blue diamond) or extrusion blown (red square) films.





100 80 Haze (%) 60 40 surface bulk 20 0 barefoot standard NS PSD-2 NS calcined kaolin 100 80 surface 60 Haze (%) 40 20 0 5 10 15 0 20 Filler loading (wt%)

Figure 8: Haze of antiblock (right) and thermal films (next column) depends on the particle size: usage of smaller particles results in better haze, especially at higher filler loadings.



Another optical film property that is affected by both particle size and PSD shape of the functional filler is the color. Not only does the mean particle size affect the color, but also the shape of the PSD. Narrower size distributions with a minimum of fine particles yield films with lower yellowness (Figure 10). Higher concentrations of sub-micron sized fines can increase the observed yellowness through a mechanism known as the Horizon effect.



Figure 10: The PSD affects the roll color of the thermal film. All films are 4-mil* thick and have 10 wt% loading.

Filler particle size distribution also strongly affects powder handling and dispersion properties. This is important not only for storage in silos, but also for feeding the filler into a compounder and dispersion in the polyolefin. The size distribution can be engineered to improve the flow properties (Figure 11). Better flow is expected to result in improved material handling and dispersion during the extrusion process.



since there is a convex interface going from air to film and visa versa. The haze can be separated into bulk and surface contributions. The surface contributes substantially more to the haze than the bulk, especially at high filler loadings such as in thermal films (Figure 9).



Figure 11: Powder flow properties are strongly affected by the filler PSD.

This combination of absorptive properties, surface area and micro-porosity correlates directly with additive efficiency. Non-reactivity with other additive components means improved cost effectiveness and performance of slip additives, antioxidants, stabilizers, colorants and other processing aids. In some formulations, MINBLOC operates synergistically with erucamide slip additives to optimize both slip and antiblock performance and to enhance film production and handling properties. Compared to more porous mineral additives, MINBLOC will not diminish the performance of costly processing aids, effectively increasing film throughput and reducing the incidence of film surface defects. Low surface area and minimal porosity also helps to reduce interference with UV stabilizers to extend the effectiveness of these important thermal film additives.

Conclusion

The effect of mineral additives on polyolefin film properties is a function of mineral composition and size distribution. This paper demonstrates how these effects can be optimized by using nepheline syenite additives with engineered particle sizes. Applications highlighted were packaging and horticultural films.

Clarity is optimized when the refractive index of the mineral matches that of the host polymer. Median particle size is also important, with finer particle sizes yielding reduced film haze. This effect is primarily due to reduced surface roughness of films using finer particle-sized mineral additives.

Antiblocking in packaging film and thermicity in horticultural film can be optimized through control of the particle's mean size and distribution. Optimal d50 values for nepheline syenite used for antiblocking and thermicity applications are approximately 7 and 10 microns, respectively. Narrow particle size distributions result in improvements in particle flow and reduced yellowness of films. Novel aesthetic effects are observed with a unique new synthetic mineral additive.

¹Petrothene[®] is a registered trademark of LyondellBasell *1 mil = one thousandth of an inch = 25.4 micron

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