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Flowabitity of Halogen-Free Flame Retardant Polymeric Compositions

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In this work we have characterized one particular type of halogen-free flame retardant polymeric composition, used as sheath of electrical wires and cables. The five pure powders used were Surlyn™9320 (ionic thermoplastic), Elvax™265 (thermoplastic - vinyl acetate and ethylene copolymer - EVA), Martinal™OL104 ($Al(OH)_3$ - halogen-free flame retardant), Cloisite™20A (organoclay) and Irganox™1010 (phenolic antioxidant). Nine premixes were also formulated using these pure components by a design of experiments known as CCRD (Central Composite Rotational Design). In all premixes prepared, the mass ratio of Cloisite™ 20A to Irganox™1010 was constant. Commercial Elvax™265 and Surlyn™9320 pellets were previously cryogenically fragmented with dry ice in a cutting mill. The flow properties of pure powders and premixes were determined using the rotational shear cell accessory of the FT-4 powder rheometer at four different consolidation conditions. The following decreasing order of cohesion for pure powders was established: Martinal™OL104 ~ Cloisite™20A > Elvax™265 > Surlyn™9320 > Irganox™1010. All premixes planned were classified as cohesive powders. The flow properties average values of the premixes such as cohesion, unconfined yield strength and internal friction among particulates as well as the compressibility percentage were dependent on mass ratio of $Al(OH)_3$ to polymeric total fraction in certain consolidation stress. All flow properties were also dependent on consolidation stress, except the angle of effective internal friction (EAIF). The flow function (FF) average values of ELVAX™ 265 presented anomalous variations regarding the levels of applied consolidation stress. The variability of the flow properties was associated to stick-slip and relaxation phenomena mainly due to sticky and elastic characteristics of the EVA particles. The $Al(OH)_3$ particles (Martinal™OL104) have actuated as anti-tack of Elvax™265. Consequently, the anomalous variability of the flow function average values disappeared for the nine premixes.

1. Introduction

Many thermoplastic materials used in electro-electronic products manufacturing have flame retardants (FR) incorporated in its compositions. The eco-friendly halogen-free flame retardants more used are $Al(OH)_3$ and $Mg(OH)_2$ that suffer an endothermic decomposition with water liberation reducing temperature surface during the fire (Liu et al. 2014).

Nowadays, worldwide health organizations are pushing plastic industry to use halogen-free compounds (Abarca et al., 2011). In Europe, there are specifics European regulatory directives that imposes the use eco-friendly products. The restrictions are based on the fact that halogen-free products are more sustainable than the traditional halogenated flame retardants that act in synergism with Sb_2O_3 resulting in polymeric composites extremely toxics (Waaijers et al., 2013). However, the expansion speed of halogen-free compounds has been limited by technological barriers linked to problems of high melt viscosity, aggravated by high concentrations of $Al(OH)_3$ and its limited thermal stability during extrusion, as well as due to low flowability of premixes in feed hoppers (Herbiet, 2008).

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By personal experience, the low flowability of halogen-free flame retardant polymeric premixes highly filled with ultrafine $Al(OH)_3$ particles reduces the productivity of the compounding process performed in two screw extruder. This is due to the spontaneous formation of stable arches in the hopper bottom, obstructing the feed flow. Consequently, the high cost of commercial halogen-free polymeric composites and the cited technologic difficulties have delayed the substitution in large scale of halogenated products in emergent countries such as Brazil. Few studies concerning this problem were carried out, using a certain fixed wire and cable sheath composition, as first approach, to provide better understanding of the poor flowability of this sort of materials (Ivanfy et al., 1987). Some conclusions revealed that flow properties of halogen-free flame retardant polymeric premixes are a decisive factor to understanding the behavior into a feed hopper, once the major problem in operating an extruder is to keep the feed ratio constant during its operation. Geometry and pressure of the feed hopper and also differences on premixes compounds, such as its size and nature, could change feed ratio and compromise the product quality and productivity.

In bulk solids field, the flowability of particulate materials is governed by its cohesion. The classification of particulate material as cohesive, easy-flowing and free-flowing powder is the well-known criterion reported by Jenike (1980), based on the flow function intervals determined for particulate materials consolidated under standardized conditions.

The shear cells are equipment able to produce states of stress quite defined which can be represented through Mohr's circles and to quantify powder's cohesion under pseudo-static conditions (Abatzoglou and Léonard, 2011). The powder particles friction against hopper wall is also a key factor to be considered and it can be measured by shear experiments (Jenike, 1980).

However, different factors such as the climatic variations (relative moisture, temperature) (LePree, 2013), transport and storage conditions could affect flow properties becoming more critical for hygroscopic materials.

The main objective of this paper was to investigate compositional effects on flow properties of the halogen-free polymeric premixes, characterized by shear experiments, and also to identify the main components of premixes that controls its flowability. Therefore, premixes composition variations were planned by a design of experiments known as Central Composite Rotational Design (Box et al, 1978).

2. Materials and Methods

2.1 Materials

Surlyn™9320 (Du Pont, USA), Elvax™265 (Du Pont, USA), Hydroxide aluminum (Martinal™OL104, Martinswerk, Germany), Cloisite™20A (Southern Clay, USA) and Irganox™1010 (BASF, Germany) were utilized as pure powders for preparation of the halogen-free premix compositions.

2.2 Cryogenic Grinding of the Polymeric Pellets

The Surlyn™9320 and Elvax™265 pellets were conditioned into thermal box with dry ice (- 80 °C). Polymers pellets were fed into a cutting mill (Marconi, Brazil) provided with a 1 mm screen outlet. Dry ice was added to the mill to avoid excessive heating during milling process. The resulting powders, after two days of natural degassing at room temperature, were stored in plastic flasks.

2.3 Experimental Design of Halogen-Free Polymeric Premixes

The central composite rotational design (CCRD) was used to evaluate the composition effects on flow properties of halogen-free polymeric premixes, containing five components. This design, resulting in the formulation of nine premixes, allowed the determination of two individual effects (R_1, R_2), an interaction ($R_1 \times R_2$) and two quadratic effects (R_1^2, R_2^2). Table 1 contains two mass ratio coded levels: Surlyn™9320 to Elvax™265 (R_1) and $Al(OH)_3$ to the sum of Surlyn™ and Elvax™ (R_2). In all compositions proposed, the Cloisite™20A to Irganox™1010 ratio (R_3) was maintained constant and equal to 2. (R_3). The lower and upper coded limits in Table 1 correspond to the following minimum and maximum mass percentage intervals: 3.6 - 8.6 % of Surlyn™9320, 30.5 % - 37.6 % of Elvax™265 and 55.0 - 61.0 % of aluminum hydroxide (Ivanfy et al., 1987).

2.4 Preparation of Halogen-free polymeric premixes

All materials utilized were previously dried at 40 ºC by 24 h before preparing the premixes. The mass of the two polymers grounded and the three non-polymeric components used for premixes formulation are in Table1.

2.5 Flow Properties of Halogen-free polymeric premixes

The nine halogen-free polymeric premixes and the five individual compounds were characterized into a shear cell accessory provided with the FT4 rheometer (Freeman Technology). The same sample of each premix was consolidated in a 85 mL and 50 mm diameter glass vessel at 3 kPa, 6 kPa, 9 kPa and 15 kPa normal stress. For each shear experiment, a yield locus comprising 5 shear points was determined twice, at 5 equidistant normal stresses in a range of 1/3 to 3/4 of normal consolidation stress. Therefore, an yield locus and its both

Mohr's circles (consolidation and unconfined circles) of each sample was then obtained and some others powder flow properties could be estimated: cohesion, unconfined yield strength (UYS), major principal stress (MPS), flow function (FF), angle of internal friction (AIF), and the effective angle of internal friction (EAIF). Compressibility (CBS) of each sample was determined by sample volume percentage reduction at 15 kPa.

2.6 Statistical Analysis of Experimental Data

The compositional effects were analyzed from regression coefficients (B_0, B_1, B_2, B_{12}, B_{11}, B_{22}) estimated by multiple regression analysis using STATISTICA Software (version 7.1). The adjusted polynomial of the flow properties estimated (y) as a function of the compositional ratios (R_1 and R_2) are presented in generic form by the quadratic equation:

$$y = B_0 + B_1R_1 + B_2R_2 + B_{12}R_1R_2 + B_{11}R_1^2 + B_{22}R_2^2 \quad (1)$$

The coefficients $B_1; B_2$ and $B_{11}; B_{22}$ are linear and quadratic terms, respectively, whereas B_{12} is binary interaction. The B_0 correspnds to average value of the flow property. The standard errors (±SE) of each regression coefficient was defined as $SE = \sqrt{MS_E C_{ij}}$. Here MS_E is the medium quadratic error estimated from the variance analysis of a given flow property and C_{ij} is the element diagonal of $(\boldsymbol{X}'\boldsymbol{X})^{-1}$ corresponding to a given regression coefficient (Montgomery, 1997). The significance of the regression coefficients was individually analyzed applying t-Student's test for significance level (p) ≤ 0.05, t-calculated was defined as ratio of each coefficient to SE. The t-tabulated was estimated with three degree of freedom resulting from difference between the total degree of freedom number (experiment total number) and the degree of freedom number used for the calculation of all coefficients. The flow properties of the five individual components were done in duplicates and their average values and the standard deviations (±SD) estimated.

Table 1: Experimental design of halogen-free polymeric compositions

Premixes	Coded levels (compositional ratios: R_1, R_2 e R_3)		
	$R_1 = \frac{\text{Surlyn}^1}{\text{Elvax}^2}$	$R_2 = \left(\frac{\text{Al(OH)}_3{}^3}{\text{Elvax+Surlyn}}\right)$	$R_3 = \frac{\text{Cloisite}^4}{\text{Irganox}^5}$
1	-1 (0.125)	-1 (1.33)	(2)
2	+1 (0.250)	-1 (1.33)	(2)
3	-1 (0.125)	+1 (1.59)	(2)
4	+1 (0,250)	+1 (1.59)	(2)
5	0 (0.1875)	0 (1.46)	(2)
6	$-\sqrt{2}$ (0.0991)	0 (1.46)	(2)
7	$+\sqrt{2}$ (0.2759)	0 (1.46)	(2)
8	0 (0.1875)	$-\sqrt{2}$ (1.2762)	(2)
9	0 (0.1875)	$+\sqrt{2}$ (1.64)	(2)

[1]Surlyn™ 9320: ethylene acid acrylate terpolymer (EAA) containing neutralized partially carboxyl groups with zinc;
[2]Elvax™ 265: ethylene and vinyl acetate copolymer with 28 wt% vinyl acetate.
[3]Hydroxide aluminum (Martinal™ OL104): halogen-free flame retardant;
[4]Organoclay based on montmorillonite intercalated with dimethyl dehydrogenated tallow ammonium quaternary chloride; [5]phenolic antioxidant.

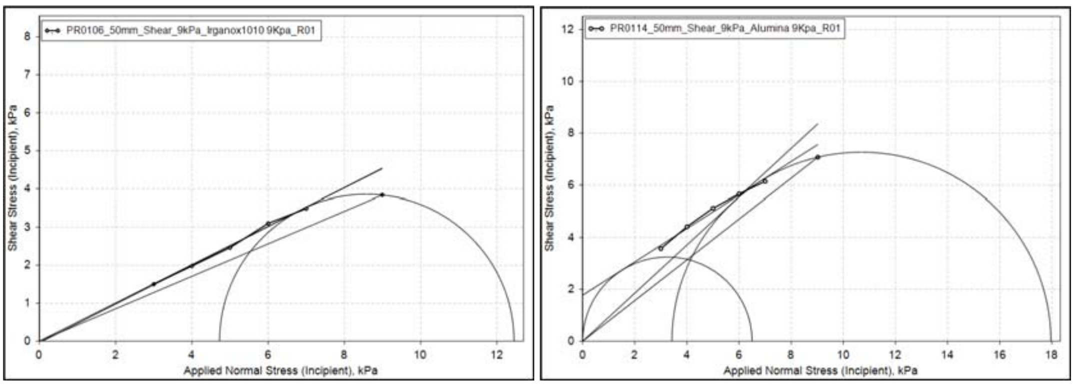

Figure 1: Mohr's circles of Irganox™1010 (left) and Martinal™OL104 ($Al(OH)_3$ - right) at 9 kPa consolidation stress.

3. Results and Discussion

The Jenike's classification, using flow function (FF) intervals, of the nine premixes planned in Table 1 and their five individually components (Table 4) were presented in Table 2. Notice that independently of consolidation nominal stress, the aluminum hydroxide (Martinal™OL104) and organoclay (Cloisite™20A) were classified as cohesive powders. On the other hand, the Irganox™1010 (phenolic antioxidant) was classified as a free-flowing powder. This was confirmed comparing Irganox™1010 and $Al(OH)_3$ Morh's circles (Figure 1) at 9 kPa. It can be seen that the Irganox™1010 presents only the major Mohr circle and the yield locus passes near by the origin (Figure 1). It represents the typical behavior of free flowing powder which significantly differs of the cohesive behavior presented by the $Al(OH)_3$ particles (Martinal™OL104) at 6 kPa and 9 kPa (Table 2).

Table 2: Classification for the halogen-free polymeric premixes and individual components according flow functions values at different consolidation stress.

Flow Function (FF)	Powder Classification	Normal load of the premixes and of theirs individual commercial components			
		3 kPa	6 kPa	9 kPa	15 kPa
2 < FF < 4	Cohesive powder	Premixes 1 to 9 Martinal™OL104 Cloisite™20A Elvax™265	Premixes 1 to 9 Martinal™OL104 Cloisite™20A	Premixes 1 to 9 Martinal™OL104 Cloisite™20A Elvax™265	Premixes 1 to 9 Cloisite™20A
4 < FF < 10	Easy flow powder	Surlyn™9320	Elvax™265 Surlyn™9320	Surlyn™9320	Martinal™OL104 Surlyn™9320 Elvax™265
FF > 10	Free flow powder	Irganox™1010	Irganox™1010	Irganox™1010	Irganox™1010

Table 3: Statistical analysis of the compositional effects on the flowability of halogen-free polymeric premixes.

Property (at normal load of)	Dimensional Unit	Average value B_0	Standard error ($B_0 \pm$ SE)	t-Student (calculated) (B_0 / SE)	Significance levels (B_0, p≤0,05)	Poly. Coefficients (B_1, B_2, B_{11},B_{12}, B_{22})
Cohesion(3kPa)	kPa	0.84	±0.14	6.03	0.009143	NS
Cohesion(6kPa)	kPa	1.32	±0.10	12.51	0.001100	NS
Cohesion(9kPa)	Kpa	2.02	±0.25	7.92	0.004191	NS
Cohesion(15kPa)	kPa	2.84	±0.14	10.09	0.002072	NS
UYS (3kPa)	kPa	3.46	±0.50	6.88	0.006289	NS
UYS(6kPa)	kPa	5.83	±0,54	10.79	0.001704	NS
UYS(9kPa)	kPa	8.43	±1.06	7.93	0.004182	NS
UYS(15kPa)	kPa	11.78	±0.97	12.16	0.001196	$-1,91R_2^2$
FF(3kPa)	-	2.25	±0.69	3.27	0.046725	NS
FF(6kPa)	-	2.69	±0.24	11.1	0.001568	NS
FF(9kPa)	-	2.70	±0.52	5.16	0.014119	NS
FF(15kPa)	-	3.31	±0.,64	5.18	0.013961	NS
AIF(3kPa)	degree	38.3	±2.8	13.46	0.000887	NS
AIF(6kPa)	degree	39,6	±1.3	31.54	0.000070	$+2,0R_2$
AIF(9kPa)	degree	38.9	±0.77	50.66	0.000017	$+1,60R_1^2$
AIF(15kPa)	degree	38.5	±2.3	16.77	0.000461	NS
EAIF(3kPa)	degree	50.3	±1.3	40.04	0.000034	NS
EAIF(6kPa)	degree	49.1	±1.3	37.04	0.000043	NS
EAIF(9kPa)	degree	48.4	±0.9	51.58	0.000016	NS
EAIF(15kPa)	degree	46.1	±1.6	29.22	0.000088	NS
CBD(aerated)	g/cm³	0.89	±0.12	7.29	0.005334	NS
Compres.(15kPa)	%	29.37	±0.25	1114.82	0.000001	$+0,85R_2-0,61R_2^2$

NS: Statistically non-significant (p > 0.05)

Independently of the consolidation stress, the grounded Surlyn™9320 was classified as an easy flowing powder (Table 2). The macromolecular structure of Surlyn™9320 contains partially neutralized carboxyl groups interconnected by the Zn^{2+} ions which act like temporary crosslink at room temperature (Coleman et al, 1990), reducing the tendency of self-adhesion between its particles. The ground Elvax™265 has presented flow function average values oscillations, changing cohesion classification depending on the normal consolidation stress (Table 2). At 6 kPa and 15 kPa consolidation stresses, the Elvax™265 was classified as a easy-flowing powder whereas it became an cohesive powder at 3kPa and 9kPa (Table 2). Although Elvax™265 has been cooled by dry ice during grinding process, the produced particles heated up. This probably favored the formation of rubbery agglomerates because Elvax™265 has a glass transition temperature below room temperature, which represents a rubbery amorphous phase. Consequently, this makes this copolymer particles be intrinsically sticky and elastic when compared to Surlyn™9230 particles behavior. This condition has led to stick-slip and relaxation phenomena (Benedek, 2004). The relaxation phenomenon happens due to internal stress created by dissipative elastic deformation of polymeric particles that temporally relax through plastic deformation. Other effects investigated as causes of the flow measurement variations are the static charge induced by friction of dielectric particles (e.g. polymer), as well as the contamination of the vessel internal wall for certain lubricant substances (Abatzoglo and Léonard, 2010). Such event might justify the inconsistent classification of $Al(OH)_3$ that presented easy-flowing behavior at 15 kPa stress, and assumed the behavior of highly cohesive powder at 3 kPa (Tables 2 and 3). In spite of the high variability (Table 4), it was possible to establish the following decreasing order of cohesion for the pure powders: Martinal™OL104 ~ Cloisite™20A > Elvax™265 > Surlyn™9320 > Irganox™1010. In addition, premixes from 1 to 9 were all classified as cohesive powders (Table 2).

It was observed a significant dependence between AIF average values and compositional ratios, expressed by two significant polynomial coefficients: linear coefficient (B_2) and two quadratic coefficients (B_{11}) that depended on consolidation stress as showed on last column of Table 3. At 6 kPa and 9 kPa of consolidation stresses, the AIF changed as a function of R_2 and of the quadratic compositional effects (R_1^2), respectively. Besides, the effective angle internal friction average values (EAIF) presented a significant negative correlation with the cohesion average values (table 3, B_o). It means that the cohesion average values of the premixes increased as function of the consolidation stress, leading to a reduction of its average effective internal friction values (Table 3), as expected. On the other hand, the AIF average values, not shown in table 4, measured for Surlyn 9320, Elvax 265, Martinal OL104 and Cloisite 20A, oscillated anomalously when consolidation stress increased. This abnormal variation can be exemplified, through the variations of EAIF average values, estimated from measures in duplicates of ELVAX™ 265 consolidated beds at 3, 6, 9 and 15 kPa (Table 4).

Table 4: Properties and respective standard deviation of individual components at different consolidations.

Material	Consoli-dation stress (kPa)	Cohesion (±SD) (kPa)	UYS (±SD) (kPa)	MPS (±SD) (kPa)	Flow Function (±SD)	EAIF (±SD) (°)
Surlyn 9320	3.0	1.1(±0.2)	3.5(±0.5)	ND	ND	ND
	6.0	0.8(±0.2)	3.0(±0.3)	13.2(±0.1)	4.5(±0.4)	40.9(±0.5)
	9.0	1.2(±0.1)	4.4(±0.1)	18.6(±0.1)	4.2(±0.1)	39.8(±0.7)
	15.0	1.83	6.87(±0.07)	28.7(±0.3)	4.2(±nd)	38.3(±2.7)
Elvax265 (EVA)	3.0	0.6(±0.2)	2.4(±0.4)	6.85(±nd)	2(±2)	24(±nd)
	6.0	0.3(±0.1)	1.5(±0.4)	12.9(±0.3)	9(±3)	45(±2)
	9.0	1.12(±0.06)	4.5(±0.2)	19.4(±0.6)	4.3(±0.3)	43.1(±0.1)
	15.0	1.0(±1)	7.95(±ND)	33(±3)	4.6(±ND)	39.9(±0.7)
Martinal OL104 ($Al(OH)_3$)	3.0	0.85(±0.06)	3.3(±0.1)	6.46(±0.09)	1.97(±0.05)	50(±1)
	6.0	1.5(±0.1)	5.4(±0.4)	12.25(±0.05)	2.3(±0.1)	46.0(±0.8)
	9.0	1.84(±0.06)	6.8(±0.3)	17.98(±0.06)	2.7(±0.1)	43.5(±0.7)
	15.0	1.7(±0.3)	7.0(±1)	28.7(±0.2)	4.3(±0.7)	42.71(±0.01)
Cloisite 20A	3.0	0.68(±0.3)	2.5(±0.2)	5.7(±0.1)	2.3(±0.2)	45.0(±0.7)
	6.0	1.0(±0.3)	3.7(±0.5)	10.73(±0.07)	3.0(±0.5)	33(±1,0)
	9.0	1.82(±0.3)	6.8(±0.2)	16.5(±0.2)	2.44(±0.05)	45.3(±0.3)
	15.0	2.6(±0.2)	10.2(±0.8)	27.4(±0.2)	2.7(±0.2)	45.8(±0.3)
Irganox 1010	3.0	0.07(±0.03)	0.2(±0.03)	4.27(±0.02)	24(±9)	28.3(±0.6)
	6.0	0.04(±0.05)	0.2(±0)	8.36(±0.01)	32(±0)	27.4(±0.2)
	9.0	-0.09(±0.05)	ND	12.52(±0.07)	ND	27.1(±0.3)
	15.0	-0.2(±0.1)	ND	20.54(±0.09)	ND	26.9(±0.2)

ND: None determinated.

It was also modeled the significant dependence of the unconfined yield strength and compressibility percentage, measured at 15 kPa as a function of compositional ratio, R_2, expressed by linear term,B_2R_2, and its negative quadratic term ($B_{22}R_2^2$) (last column, Table 3). This means that premix consolidated beds at 15 kPa, which presented the lowest compressibility and unconfined yield strength average values, contain lower levels of $Al(OH)_3$. However, the studied compositional effects on UYS average values were not significant at 3 kPa, 6 kPa and 9 kPa consolidation stress, according to Table 3. The cohesion not depended on R_1 and R_2 compositional ratios, but was significantly affected by the consolidation stress applied (Table 3).
In conclusion, the adherence of $Al(OH)_3$ ultrafine particles on polymer surfaces should reduce the sticky character of the rubbery agglomerates mainly attributed to the presence of Elvax™265. For this reason, the $Al(OH)_3$ was unique compositional variable which partially explained the variations of UYS, AIF and CBS in certain consolidation nominal stress given in Table 3. The anomalous flow function average values variations for the pure powders (Table 2 and 4), as observed for Elvax™265, evidenced that $Al(OH)_3$ produced an anti-tack effect between the particles of this copolymer.

4. Conclusion

A cohesion decreasing order for the premixes and their pure components was established. The flow behavior of Irganox™1010 was typically free-flowing whereas the major component of the premixes, $Al(OH)_3$, varied from highly cohesive to easy-flowing with increasing consolidation stress. All flow properties were dependent on the normal consolidation stress, except the effective angle of internal friction (EAIF). The premixes flow properties, such as, cohesion, unconfined yield strength, angle of internal friction and compressibility have presented a statistically significant dependence on the mass ratio of $Al(OH)_3$ to polymeric total fraction, but limited to a certain consolidation stress applied. The flow function (FF) average values of the Elvax™265 presented anomalous variations regarding the levels of applied consolidation stress. The variability of the flow properties was associated to stick-slip and relaxation phenomena mainly due to the sticky and elastic characteristics of EVA particles (Elvax™265). The $Al(OH)_3$ particles have actuated as anti-tack of the Elvax™265. Such anomalous flow function behavior was not observed for the nine formulated premixes.

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