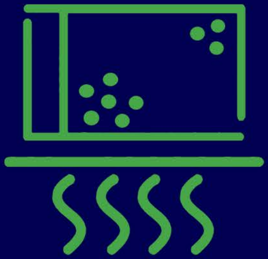

FOAMS® 2021

September 13-16, 2021 • Virtual Conference

Presented by SPE Thermoplastic Materials & Foams Division

Conference Proceedings

NOVEL ETHYLENE BASED TERPOLYMER FOAMS

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Abstract

Foams made of ethylene-vinyl acetate copolymers (EVA) are widely used for different applications such as footwear, toys, carpets, sports equipment, etc. However, EVA foams usually do not exhibit a good balance of mechanical properties at lower hardness. Thus, new materials are being developed in order to circumvent this problem. In this work, a comprehensive compositional study was performed on foams made with new-to-the-world ethylene based terpolymers. Design of experiments along with regression and variance analysis were used in order to understand the effects of terpolymer chemical composition, blending with EVA, peroxide and chemical foaming agent contents over properties such as hardness, density, rebound resilience, compression set and uniaxial tensile strength. Observed trends related to the formulation components in the raw data were same as the ones predicted in the literature and the statistical tool. In addition, important interactions between factors (peroxide and CFA contents; chemical composition of the terpolymer and blending with EVA), were detected through the regression analysis.

Introduction

EVA foams

Polymer based foams are continuously gaining technical and commercial importance due to their light weighting capabilities. Due to their excellent balance in properties, these foams are used in a wide range of applications such as automotive, packaging, footwear, construction, etc. [1].

EVA foams, one of the most important families of polymer based foams, can be produced via different processes, such as extrusion, injection molding, compression molding, etc. Depending on the end use, these foams can be crosslinked. Crosslinking of EVA foams allows the cells to stabilize during foaming upon heating in compression and injection molding. Two main crosslinking methods are physical (e.g. electrons or gamma irradiation) or chemical crosslinking (using free-radical generating agents such as organic peroxides). Similarly, foaming can be obtained with a physical (direct gases injection, such as N2 or CO2) or chemical route (using agents such as azoderivatives that decomposes and release N$_2$ gas). [2]

Properties of EVA foams are directly related to the base polymer. VA content is a key governing factor of EVA properties. The higher the VA content, the less crystalline and softer is the polymer, losing all crystallinity at about 50 wt% of VA. [3]

Novel terpolymers

The new ethylene based terpolymers consists of ethylene, vinyl acetate (VA) and a third co-monomer, randomly distributed along the backbone. The third co-monomer was added to EVA structure to improve its performance. The novel terpolymers (herein named DV001A and DV001B) had a total co-monomer content close to 33 wt%, while the degree of vinyl acetate was higher for DV001A.

Experimental

A full multilevel factorial experiment was performed using Minitab® 19.2020.1 (64-bit) software, in one replication, considering four factors, with the variation of two levels (-1 and 1) for terpolymer chemical composition (different degrees of vinyl acetate substitution), peroxide and chemical foaming agent (CFA) contents, and three levels (-1, 0 and 1) for blending with EVA with 28 wt% VA, totalizing 24 experiments (Table 1). A randomized form of the experiment was followed since it diminishes chances of misinterpreting effect of factors in a study with factors that are not being considered, especially time dependent effects. [4-6]

Table 2: Full multilevel factorial experiment of formulations for the studied foams.

Sample	Polymer	Blend - HM728	A[O]	Blowing agent
1	DV001A	-1	-1	-1
2	DV001A	-1	-1	1
3	DV001A	-1	1	-1
4	DV001A	-1	1	1
5	DV001A	0	-1	-1
6	DV001A	0	-1	1
7	DV001A	0	1	-1
8	DV001A	0	1	1
9	DV001A	1	-1	-1
10	DV001A	1	-1	1
11	DV001A	1	1	-1
12	DV001A	1	1	1
13	DV001B	-1	-1	-1
14	DV001B	-1	-1	1

15	DV001B	-1	1	-1
16	DV001B	-1	1	1
17	DV001B	0	-1	-1
18	DV001B	0	-1	1
19	DV001B	0	1	-1
20	DV001B	0	1	1
21	DV001B	1	-1	-1
22	DV001B	1	-1	1
23	DV001B	1	1	-1
24	DV001B	1	1	1

A base formulation was developed for the experiments, which contained 100 phr of polymer, 10 phr of mineral filler, 2 phr of zinc oxide, and 1 phr of stearin. The role of metal oxide and stearin is to lower the activation temperature of the CFA. Mineral fillers in foam formulations have several roles such as increasing stiffness (which is not always desired) and thermal resistance, but mainly, decreasing the overall cost of the formulation. [7,8] The recipe is based on standard formulations for commercial foams and variation of the ingredients is beyond the scope of the present work.

The contents selected for peroxide, chemical foaming agent (CFA) and EVA blending were also based on the range of usual industrial formulations, Table 2. Peroxide content was normalized to its active oxygen content.

Table 2: Contents (in phr when applicable) of the variables analyzed in our DOE.

Component	Level -1	Level 0	Level 1
Polymer type	DV001A	-----	DV001B
Blend with EVA (wt%)	0	30	70
CFA (phr)	1,5	-----	3
Active Oxygen (phr)	0,064	-----	0,083

Materials

DV001A (total co-monomer of 33.9 wt%), DV001B (total co-monomer of 33.4 wt%), EVA HM728, (28,5 wt% VA) were supplied by Braskem. 2,2-bis (Bis-t-butyl peroxy) diisopropylbenzene (bis peroxide), azodicarbonamide (CFA), zinc oxide, and stearin were purchased from Arkema, Proquitec, Auriquímica, and Baerlocher, respectively, and used in the foam formulations.

Sample preparation

Mixing was performed in a Banbury (Quanzhou Yuchengsheng Machine CO., LTD, Model XSN-5) for 15 - 20 minutes, reaching a temperature of 115°C. All materials (except for the peroxide and chemical foaming agent) were fed in the kneader initially, and after initial dispersion, the peroxide and CFA were added. After mixing, a sheet of material with a thickness of approximately 1,7 mm was produced by a mill roll (Mecanoplast), at 50°C. After a period of 90 hours, 93 grams of the sheet was fed in a hydraulic hot press using a mold with the internal dimensions of 10 x 10 cm, external dimensions of 15 x 15 cm, and height of 1 cm, and foams were produced via compression molding with a pressure of 15 ton at temperature of 179°C, for 8 minutes.

Samples for density (disks with a diameter of 15 mm) were cut from the molded part with a hole saw. The same procedure (but with a 29 mm diameter) was used to obtain the compression set samples. The rebound resilience and hardness tests were performed on a 5 x 5 cm square, cut from a corner of the plate, and the tensile test was performed in die cut specimens (type C - ASTM D412) from cut sheets from the compression molded plates (3-4 mm thickness).

Testing

The measured properties were Hardness (Shore O - ASTM D2240); rebound resilience (pendulum, DIN 53512:2000); density by water displacement (ASTM D792); compression set @ 50% deformation, 50°C, 6 hours, with a cooling time after test of 30 minutes (ASTM D395); tensile test according to an adaptation of ASTM D638 (samples climatizing at 23 ± 2°C, 50 ± 5 % RH, test at the same conditions, test speed of 500 mm/min) where stress and strain at break were recorded.

Density experiments were conducted in triplicate, with great reproducibility, where all coefficients of variation (CV = Standard deviation*100/average) were below 2%. For hardness Shore O, 5 measurements were taken for each specimen, the average was recorded and the CV were all below 2%. Compression set were performed in duplicate, with good reproduction of all values (changes between the two runs were below 5%). For uniaxial tensile, at least 5 specimens were tested for each composition, and all CVs were below 10% for stress and strain at break and tensile modulus.

Results and discussion

In order to validate and quantify observed differences and trends, variance and regression analysis using the function “analysis of factorial experiment” of Minitab were performed. The convention for the variables is A – Terpolymer chemical composition (DV001A and DV001B); B – Blend with EVA; C - Peroxide content (A(O) - active oxygen); D – Chemical foaming agent (CFA) content. There is a normal distribution verification of the data through a normal probability plot in order to validate premises of the model. [4, 9] The p-value was evaluated in the variance analysis, meaning that if p-value

≤ α (in the present work α is 0.05), there is statistically significant correlation between the variable and its coefficient in the regression equation, and the evaluated response is statistically dependent on the variable. A visual way to rank the variables (and combination of) is through the Pareto chart, in which indexes above the reference line drawn, obtained using Lenth's method, have statistically significant effect over the response. [4] Lastly, plots of adjusted averages for both individual variables and combination of, demonstrate visually the trends of the properties.

Effect of the studied parameters over density

Analyzing the density through the Pareto chart (Figure 1) the order of importance of the variables (and combinations) follows the order: D > C > CD. Other factors and interactions do not show statistically significant effects. The analysis output is coherent to the theoretical foundation since the foaming process consists of cell nucleation and growth (and lastly, stabilization) and the amount of CFA (and therefore, the amount of gas generated) dictates the maximum possible expansion. On the other hand, content and the reaction kinetics of the organic peroxide will affect the limit of the expansion and cell growth through crosslinking, which greatly increases melt strength. The balance of cell growth vs crosslinking (among some other factors, such as the polymer density, nucleation rate, presence of fillers, etc.) will dictate the density of the foam. [10 - 12]

The interaction CD is statistically relevant possibly due to the competition between expansion and crosslinking, and all the rearranges that happen during and after compression molding. In addition, it is possible that the very presence of CFA and expansion might interfere in the crosslinking dynamics. [10]

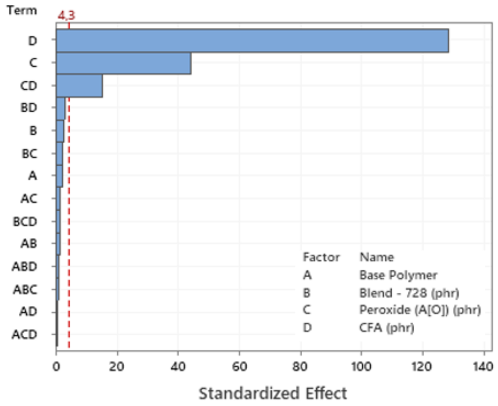

Figure 1 - Pareto chart of the variables that affect density. Reference line draw in red.

Influence of the studied parameters and their combination over density, being CFA content inversely proportional to the response, and the peroxide content, directly proportional are displayed in the main effects graph, Figure 2 a and b. Higher peroxide contents led to higher densities due to a faster and more intense crosslinking, [11, 13] therefore, restricting cell growth. Figure 2 b displays the difference in slope among curves of different variables only for the combination CD, which is in line with the variance analysis output.

Lastly, the density data show an overall normal distribution, with no violating patterns (such as S shaped curves, up or downward trend, or outliers in the edges of the dataset), validating the premise of the model, Figure 3. [4, 9] For all other properties, the plot of the residuals was very similar, and therefore, they were not displayed.

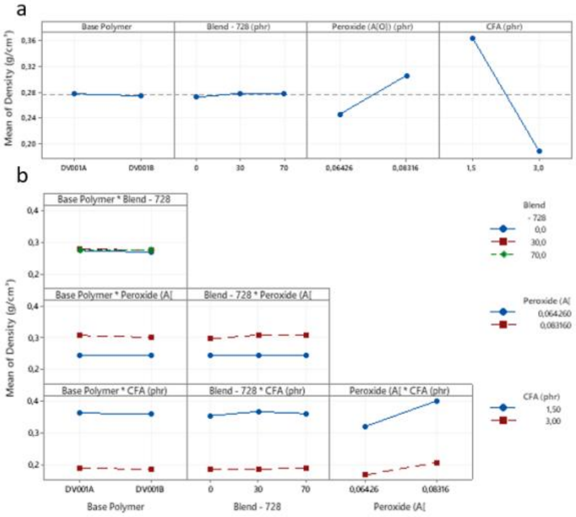

Figure 2 - a) Main effects plot for density, and b) Interactions plot for density.

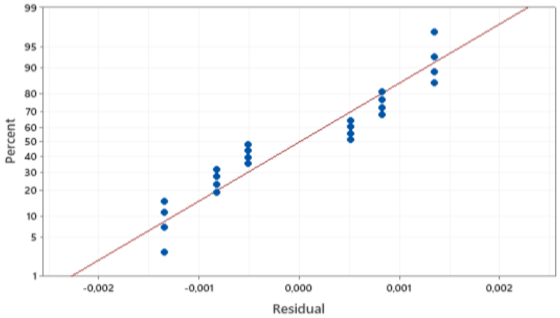

Figure 3 - Residual plot for the data of density.

Effect of formulation components over Hardness (Shore O)

For Hardness (Shore O) the sequence of importance of the variables (and combination of) is: D > C > B. All combinations and the terpolymer composition have no significant effect and this is also displayed through the variance analysis, where all p-values are above the significance level (α = 0.05) (data not shown).

The response and the proportionalities (Figure 5a) are similar to what was observed for density, possibly because it has a very strong influence over mechanical properties of foams, such as its compression, tensile and tear strength, hardness, modulus, etc., where usually, low densities lead to low hardness. [14, 15] Besides the reduction of density through cell nucleation and growth, crosslinking generally leads to an increase in stiffness and hardness of polymers. [12, 13] The presence of EVA HM728 led to an increase in hardness as well, which is coherent since it is an ethylene copolymer with a lower total co-monomer content when compared to DV001A and DV001B, and therefore, it presents higher crystallinity, and therefore, hardness. When analyzing the combinations of variables, Figure 5b, there is the indication of little influence over hardness, since the behavior of the curves corresponding to a specific content of the second variable are very alike. Lastly, in a very similar fashion to what happened for density, the hardness data seemed, normally distributed, with a good correlation of the datapoints and a straight line and only a few outliers (data not shown). [4, 9]

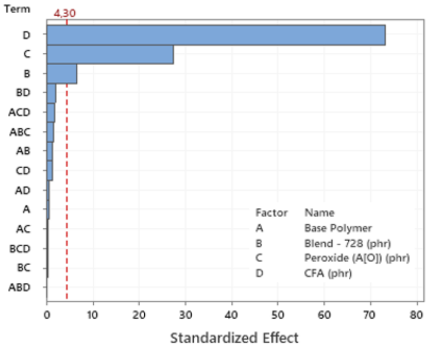

Figure 4: Pareto chart of the variables that affect Hardness (Shore O). Reference line draw in red.

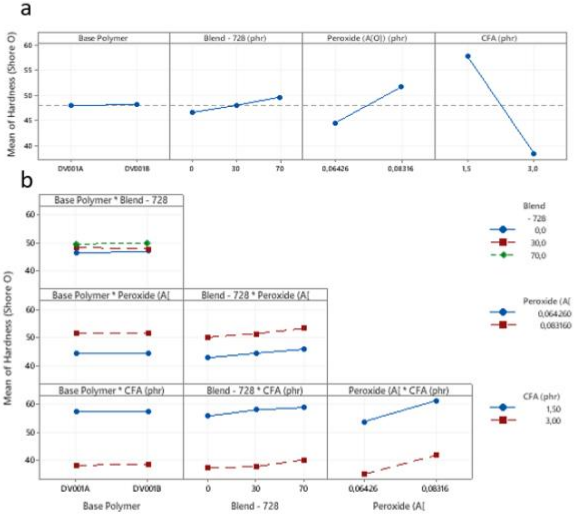

Figure 5 - a) Main effects plot for Hardness (Shore O), and, b) Interactions plot for Hardness (Shore O).

Effect of formulation components over compression set

For compression set at 50°C, 50% deformation, for 6 hours, no variable or combination of were considered statistically significant in the variance analysis – all p-Values were above 0.05. However, when looking both at the Pareto chart, Figure 6, and the main effects and interactions plot, Figure 7, it is possible to notice that the CFA content (D); the combinations of CFA and peroxide content (CD); and terpolymer composition and peroxide content (AC), are the most relevant parameters affecting compression set.

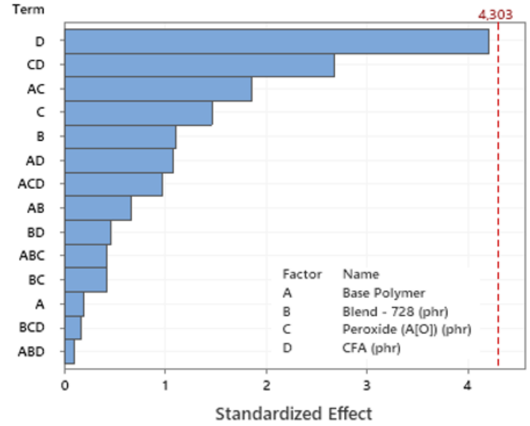

Figure 6 - Pareto chart of the variables that affect compression set. Reference line draw in red.

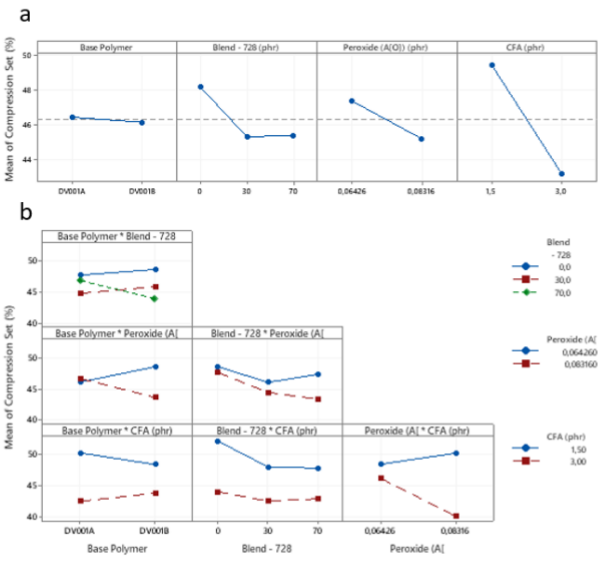

Figure 7 - a) Main effects plot for compression set, and b) Interactions plot for compression set.

According to the theoretical foundation, one would expect that in general, foams with a higher CFA content (and therefore, lower density) would present higher compression set values, because the higher gas phase fraction, as well as the usually thinner cell wall should lead to a reduction of the polymer contribution to the mechanical property and increase the probability of gas exiting the cells. [12] However, the opposite trend was observed for the tested foams.Coherently, the observed trend of decreasing CS with increasing peroxide content matches the expected, since the increase in crosslinking leads to the increase in the stiffness and hardness of the material which should diminish the plastic buckling of cells and chain slipping, and ultimately, decrease compression set. Finally, addition of EVA HM728 indicates a trend of reducing compression set. Sharma et al shows that usually, increasing vinyl acetate content in EVA should lead to an increase in elastic recovery capability for neat EVA and blends with EPDM, which should reduce compression set. [16] However, morphological aspects of the foams such as cell size distribution and wall thickness, or the crosslinking density of EVA compared to the terpolymers might be the reason to this. However, those are hypothesis, and further studies are being conducted in order to elucidate this phenomenon.

In a very similar fashion to what happened for all the other properties, CS data seems normally distributed, with a good correlation of the datapoints and a straight line and only a few outliers (data not shown). [4, 9]

Effect of formulation components over rebound resilience

For rebound resilience the sequence of importance of the variables (and combination of) is: D > AB > A, Figure 8. All other combinations, blending with EVA HM728 and the peroxide content have no statistically significant effect and this is also displayed through the variance analysis, where all p-values are above the significance level ($\alpha = 0.05$) (data not shown). This response is coherent since foam density, cell density (in other words, the amount of entrapped gas in the foam) and chain mobility (which is mainly affected by crosslinking density and crystallinity – besides the polymer chemical composition), will ultimately dictate the rebound resilience property. For foams made of polymers with more pronounced viscoelastic characteristics (which can be reduced upon excessive crosslinking), their shape will be more easily conformed when mechanically stressed, and also will recover shape more rapidly upon unloading. Lastly, foams with a higher gas volume (lower density) presents enhanced recovery. [11]

In the present study, density (and in a more complex manner, cell density) is strongly affected by the CFA content (D). In addition, changing the base polymer composition (higher content of new co-monomer for DV001B), as seen in Figure 9 a) leads to a reduction in overall molar co-monomer content (because of the higher molecular weight of the new co-monomer and also there is a difference in 0.5 wt% in total co-monomer content, being larger for DV001A), which can decrease the elastomeric response of the material.

Lastly, the combination of base polymer and blending with EVA HM728 seems to have a significant influence over resilience, as seen in Figure 9 b. However, the exact trend is not clear, since the overall trend of the change from DV001A to B is to decrease the property, and the addition of HM728 apparently leads to a decrease in resilience (when it is 30 phr), and afterwards, an increase when it is to 70 phr. Overall. the effect of density and co-monomer content found in the statistical analysis matches the theoretical foundation. [11]

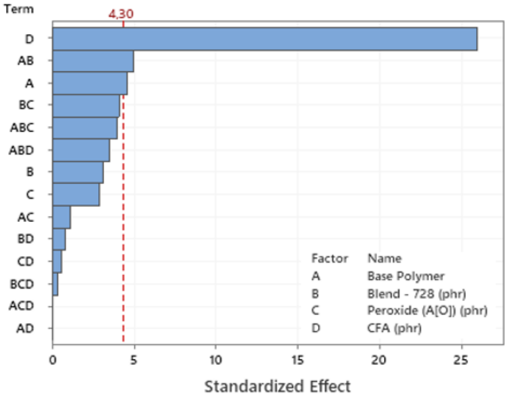

Figure 8 - Pareto chart of the variables that affect Rebound resilience (%). Reference line draw in red.

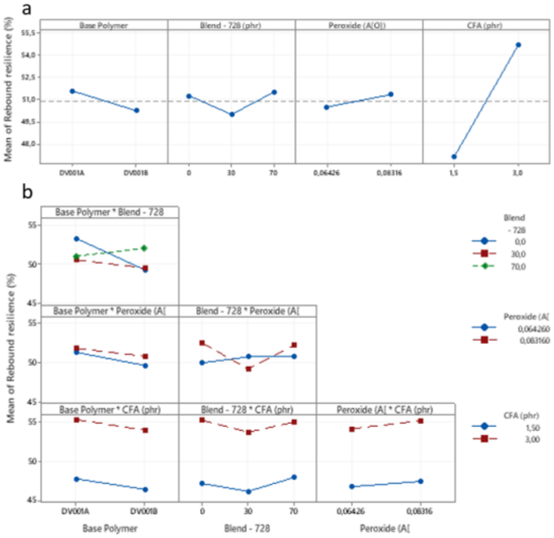

Figure 9 - a) Main effects plot for rebound resilience, and b) Interactions plot for rebound resilience.

In addition, CS data seems normally distributed, with a good correlation of the datapoints and a straight line and only a few outliers (data not shown). [4, 9]

Effect of formulation components over stress at break (uniaxial tensile)

For stress at break, no variable or combination of were considered statistically significant in the variance analysis – all p-Values were above 0.05. However, it is clear when looking both at the Pareto chart, Figure 10, and the main effects plot, Figure 11 a, that the CFA content and blending with EVA HM728 have the largest influence over the stress at break in uniaxial tensile testing. A positive correlation is seen with the blends, since EVA HM728 outperforms the neat polymers in tensile properties, while the opposite trend is observed with the increase of CFA, which is also expected due to the clear density reduction that it leads to [14, 15]. Besides, no important interactions between variables are observed, Figure 9 b, and a very small difference is observed when changing the terpolymer composition or the peroxide content. The neat terpolymers have similar performance in terms of tensile strength, and although it was not a strong factor in this analysis, the expected trend would be the increase of tensile strength (and decrease of strain at break) when further crosslinking a polymer.

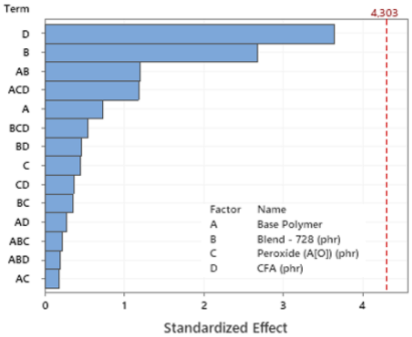

Figure 10 - Pareto chart of the variables that affect stress at break. Reference line draw in red.

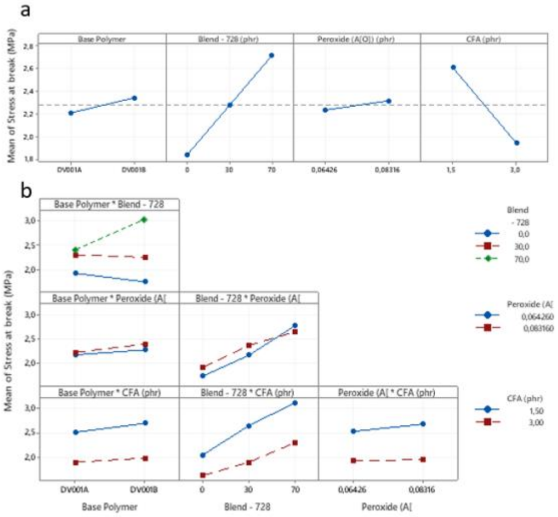

Figure 11 - a) Main effects plot for stress at break, and b) Interactions plot for stress at break.

In addition, the stress at break data seemed, normally distributed, with a good correlation of the datapoints and a straight line and only a few outliers (data not shown). [4, 9]

Effect of formulation components over strain at break (uniaxial tensile)

For strain at break, no variable or combination of were considered statistically significant in the variance analysis – all p-Values were above 0.05. However, it is clear when looking both at the Pareto chart, Figure 12, and the main effects plot, Figure 13 a, that the peroxide content, CFA content and blending with HM 728, in that order, have the largest influence over this property, being for blending a positive, and peroxide and CFA content, a negative correlation. Those trends are in line with the predicted in the literature, due to: the effect of CFA over density (whose effects have been already discussed); the effect of increasing crosslinking density, which leads to a decrease in molecular mobility, chain slipping, and therefore, strain at break; and the addition of EVA HM728, which by itself, has a larger deformation capability in tensile.

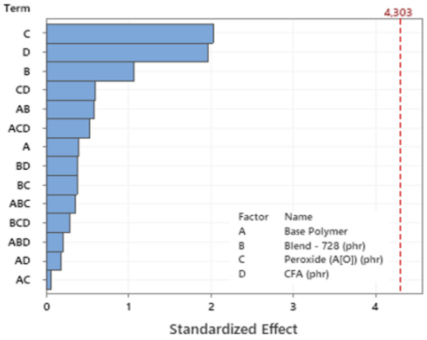

Figure 12 - Pareto chart of the variables that affect strain at break. Reference line draw in red.

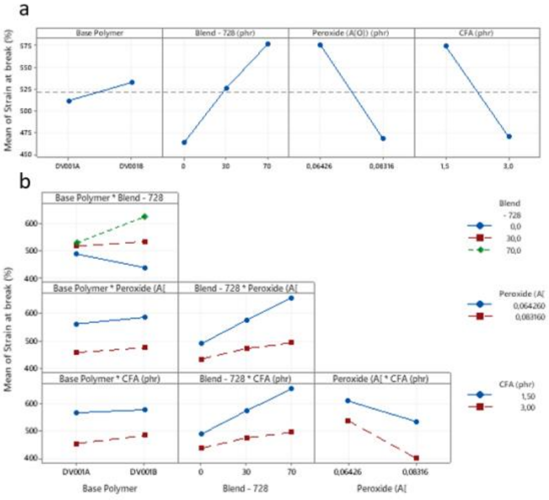

Figure 13 - a) Main effects plot for strain at break, and b) Interactions plot for strain at break.

Conclusions

The measured properties were evaluated through variance and regression analysis, where the effect of variable and combination of were tested for their statistical significance over those properties. Statistical analysis and the observation of the trends matches most of what is predicted on the literature [10-17]:

- Decrease of density, hardness, and tensile properties; and increase of rebound resilience with increasing CFA;
- Increase of density and hardness; decrease of compression set and strain at break with increasing peroxide content;
- Increase of hardness and tensile properties when blending (and increasing the content) with EVA HM728;
- Higher rebound resilience for DV001A – lower "new co-monomer" content and slightly higher total co-monomer content;

In the statistical analysis, a significant interaction between peroxide and CFA contents (CD) was detected for density, which although precited in literature [10], could not be detected simply looking into the data. Also, the interaction AB (terpolymer chemical composition and blending with EVA HM728) for rebound resilience was detect as significant. This kind of finding is one of the most relevant advantages of using statistical tools for evaluating a dataset.

Acknowledgements

This work would not be possible without the support from Braskem's Innovation and Technology area, which gave the authors freedom to complete this study. In addition, I would like to thank our analysts André Ricardo Rech, Gerson Vargas Galdino, Everton Lopes da Silva Carla Kremer and Rodrigo Brietzke from our Innovation and Technology Center at Triunfo-RS for the excellent work in the compounding and analysis of those materials, as well as ISI Polímeros from São Leopoldo-RS which provided a great service with compression molding of the foams and Tacosola from Novo Hamburgo-RS, which kindly performed the rebound resilience tests.

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