Study of the influence of the composition of the grommet on the Sticking & Stucking and Gas Loss behavior of the valves

Maria Luís V. Rodrigues

Abstract

This project is based on the research and development of aerosol valves to dispense polyurethane (PU) foam, focused in the behavior of the rubber grommet, which allows the activation of the valve. To fulfill chemical and mechanical properties requested for a polyurethane foam valve was necessary to study new compounds and solutions for the valves, resulting in two sub-projects: improvement of the standard valve and development of a new valve generation with longer shelf-life.

The shelf-life of these systems is dependent of the impermeability of the grommet to the water and of the capacity of the grommet to isolate the blowing gas inside the can. The existence of water inside these systems will promote the reaction between free NCO groups from the system with water, resulting in the formation of a harder compound, polyurea. This reaction will create a harder layer next to the valve and the grommet will be hardened in preferred locations (regions under shear stress). The hardened compound will difficult the opening of the valve, sticking and/or stucking the valve.

The chemical resistance of various types of rubbers from different suppliers was tested, gas losses with and without foam were followed and studied and other tests were performed. In particular, it was imperative to study the number of weeks after which the valve still opens, dispensing foam. After studying different rubber materials, was observed that changing fillers in rubber composition and its quantities will change rubber impermeability and chemical resistance. Neoprene® is still the best choice for polyurethane requisites.

Keywords: Aerosol Valves, Grommet, Elastomers, Polyurethane foam, Swelling, Neoprene®

1. Introduction

The essential element in every aerosol dispenser is the valve. This project is focused in the improvement of aerosol valves to dispense PU foams, where the sealing of the blowing agents trapped inside the aerosol must be improved.

A typical aerosol valve is made up from 4 components, like this example described on figure 1.

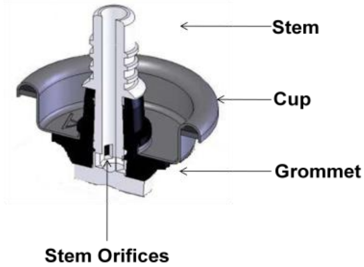

Figure 1. Aerosol valve.

The valve stem will allow the activation of the valve, which has orifices inside to allow the dispensing of the foam; the grommet made of vulcanized rubber which gives elasticity to the valve for the opening and closing of the valve, covering and uncovering the stem orifices; cup, generally made of tin plated material, which will fix the valve to the aerosol can.

This project will be focused on the study of polymer materials with rubber behavior to be used in the grommet, to improve its boundaries properties, increase its shelf-life, reduce the aging of the grommet and increase its chemical resistance. Therefore, it is important to analyze the mechanical properties and chemical resistance of these materials, to achieve a high quality grommet.

Rubber compounding is a complex, multidisciplinary science of selecting and blending the appropriate combination of elastomers and other ingredients to meet the performance, manufacturing, environmental and cost ingredients for rubber goods made and used in commerce. Compounding is a high complex science involving many traditional disciplines such as organic chemistry, polymer chemistry, materials physics, mathematics and engineering mechanics [1].

Raw materials for a compound are generally polymers, fillers, antioxidants and antiozonants, plasticizers or oils, bonding agents or adhesives (if needed) and vulcanization system. Fillers like carbon black (primary reinforcing filler in rubber industry), short fibers or flakes of inorganic materials, improve the mechanical boundary and chemical properties of a polymer material. The reinforcing fillers improve the physical properties of the rubber vulcanizate, while some filler simply act as diluents or extenders. Extenders, like silica and calcium carbonate, permit a large volume of a plastic to be produced with relatively little actual resin [1, 2].

The polymeric material used in the standard grommet is an elastomer, like the natural rubber, which meets the mechanical and chemicals properties necessary during the shelf-life of the aerosol can. The typical characteristic properties are high extensibility, non-permanent deformation, resistance to high and low temperatures and chemical resistance to the PU foams and blowing agents.

The compromise between the mechanical and chemical properties leads the study to analyze the influence on the different formulations of chloroprene rubber to achieve optimum performance. Chloroprene rubber is a polymer of 2-chloro-1,3 butadiene and its structure can be modified by copolymerizing chloroprene with sulfur, 2,3-dichloro- 1,3- butadiene, or other monomers to yield a family of materials with a broad range of chemical and physical properties. By proper selection and formulation of these polymers, the compounder can achieve optimum performance for a given end-use. Properties like degradation resistance, good performance when in contact with oils and many chemicals, wide temperature resistance and outstanding physical toughness are achieved with this vulcanized rubber [3].

2. Experimental

2.1. Materials and equipments

Ten different formulations of chloroprene were used from two different suppliers (A and B).

Supplier	Formulation	Modifications
A	F1	Standard Compound
	F2	Standard Compound
	F3	Fillers and higher vulcanization
	F4	Fillers, plasticizer and silicone
	F5	Fillers, plasticizer and silicone
	F6	Fillers and plasticizer
	F7	Fillers and plasticizer
	F8	Fillers and plasticizer
B	F9	Standard Compound
	F10	Fillers amount and size

Rubber formulation 1 and 2 (F1 and F2) are the currently vulcanized rubbers used on the standard valves.

Two foam formulations, α (lower content of blowing agents) and β (higher content of blowing agents), were used to promote different PU environments where the valve is contact with.

All work was carried out using the company equipments, raw materials to produce PU foams, components currently used to assemble an aerosol valve and the aerosol system. All the tests are realized based on the company norms.

2.2. Mechanical tests

The tensile properties and tear resistance of the rubber formulations were measured on an Instron tensile testing machine. These mechanical tests cover the determination of the radial tear strength and the snappiness of the rubber grommets.

The radial tear is performed to fifty grommet samples, while the snappiness is evaluated with five grommet samples.

2.3. Tests with PU foam

This test method covers the determination of the sealing performance and shelf-life of aerosol valves used.

Gas loss test was performed on cans filled with PU foams, α and β. For this test, five cans with PU foam were stored at two different temperatures, 23 and 45ºC, and the gas loss is measured during eight weeks.

The test to analyze the shelf-life of an aerosol valve was performed with ten cans previously filled with α and β PU foams. This test is carried out in different types of environments and aging conditions, at 23 and 45ºC. The gas loss, opening load of the valve and the quantity of foam dispensed is analyzed regularly, after two or five aging weeks (at 23 and 45ºC, respectively).

2.4. Swelling studies

A test piece weighting about 1,11 ± 0,23 g of each rubber formulation was cut from a rubber sheet. The samples were immersed in acetone, blowing agents X, blowing agents Y, blowing agents Z and MDI at room temperature during seven days to allow the swelling to reach diffusion equilibrium. At the end of this period, the trial sample was taken out and the adhered liquid was rapidly removed by blotting with laboratory paper. Afterwards the swollen weigh, dimensions and hardness were immediately measured. After three more days, the samples were measured again. The swelling ratio is defined as

$$\%\Delta V = \frac{Vi - Vf}{Vi} \times 100 \quad (1)$$

$$\%\Delta W = \frac{Wi - Wf}{Wi} \times 100 \quad (2)$$

$$\%\Delta H = \frac{Hi - Hf}{Hi} \times 100 \quad (3)$$

where V_i, W_i and Hi are, respectively, the original (unswollen) volume, initial weight and micro hardness, and V_f, W_f and H_f the final results. The %ΔV, %ΔW and %ΔH are the changes in the original sample.

3. Results and discussion

3.1. Mechanical tests

The grommet F3 showed a non-acceptable behavior, starting to tear near 10 mm of extension, inferior to the 15mm required to guarantee a good performance during production. Were tested 50 samples and only one grommet did not fail. Therefore, this grommet is not a good option because is impossible to assemble during production. F5 and F9 grommets were not good options as well. This grommet supplied by B was a promissory version but the radial tear results made this grommet an impossible option considering that during production 40% can fail. Meanwhile, working with the supplier, the compound was improved. Therefore, the tearing behavior of the new compound F10 was improved as it is shown – figure 2.

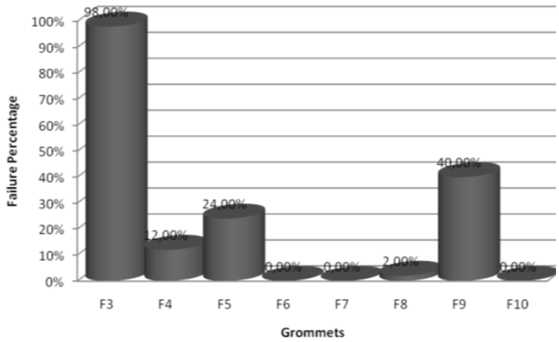

Figure 2. Tearing results from all rubbers radial tear test.

All rubber grommets showed an acceptable snappiness since the applied load necessary to open the valve was low and the area inside the lines is small, where the grommet F10 as a lower loss in its hysteresis – figure 3.

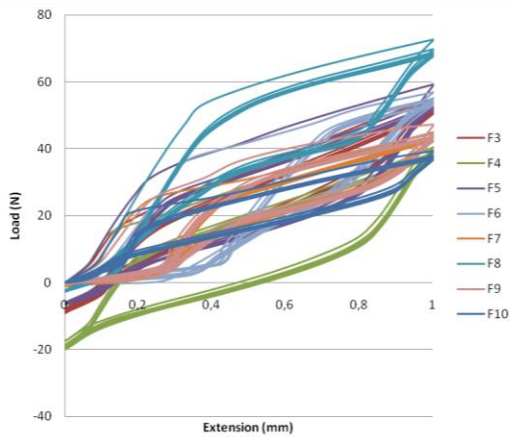

Figure 3. Snappiness results.

3.2. Tests with PU foam

The gas loss results with α-PU foam are showed on figure 4. The F10 rubber showed to be the best solution with a higher impermeability, having the lower gas loss values.

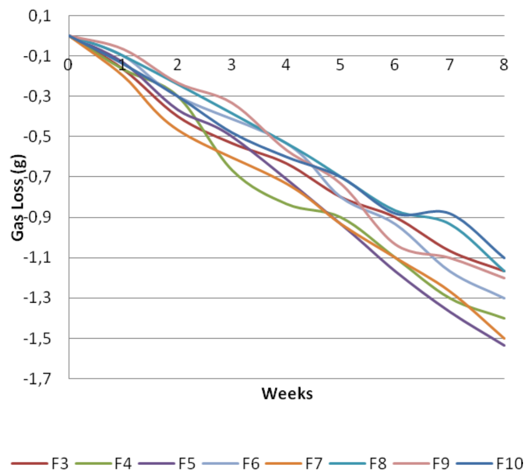

Figure 4. Gas loss results with α-PU foam.

Gas loss values with β-PU foam differ from the α-PU foam. With α-PU foam was expectable to have higher gas losses, considering that the formulation has a higher content of blowing agents. Once more, as expected, the F10 grommet is the best one having the lower gas loss between the new valves in study – figure 5. F9 and F5 rubber formulations were cancelled since the mechanical tests and gas loss performed with α-PU foam did not show any improvement.

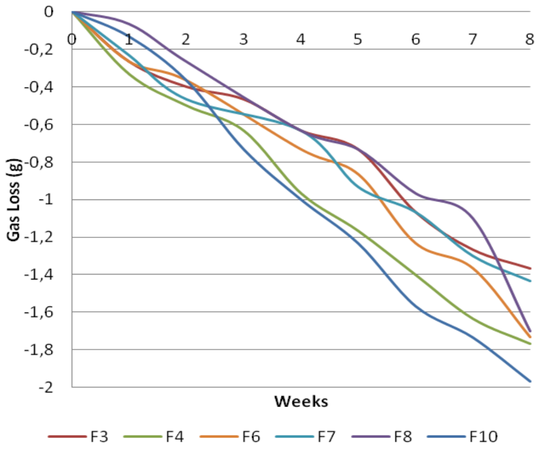

Figure 5. Gas loss results with β-PU foam.

With the F10 rubber formulation, the sticking and stucking test was performed at 23 and 45ºC, aging temperatures, with both α and β PU foams. The necessary load to open the valves is more in concordance with the foam aging evolution during the weeks at 23 and 45ºC. The aging of the foam is higher at higher temperatures.

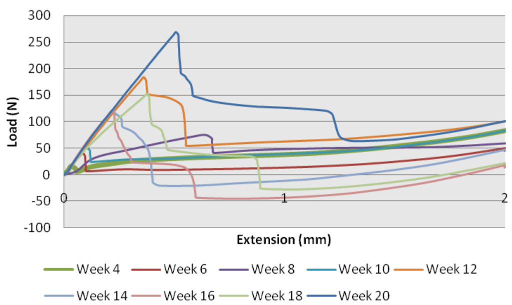

Figure 6. Opening load results at 45ºC with F10, using α-PU foam.

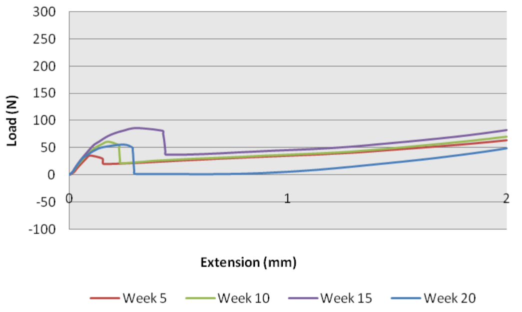

Figure 7. Opening load results at 23ºC with F10, using α-PU foam.

The opening load applied to the valve with the β-PU foam is lower than the applied load with the α-PU foam – figure 8.

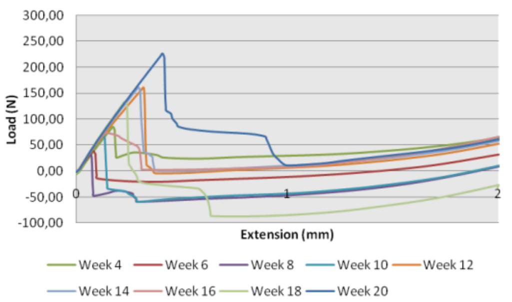

Figure 8. Opening load results at 45ºC with F10, using β-PU foam.

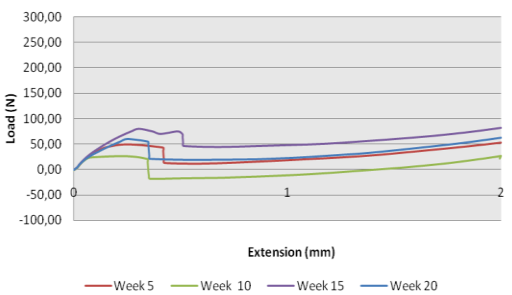

Figure 9. Opening load results at 23ºC with F10, using β-PU foam.

On the figure 10 and 11, we can observe the differences between the dispensed foam from both PU foams and, how is expected, we had higher quantity of foam results with the β-PU foam since it has more gas quantity. With the α-PU foam, the results are lower and at 45ºC we already have blocked valves, due to the foam quality and aging. The green line corresponds to the minimum acceptable quantity of foam, i.e., below 40 grams per 10 seconds the valves are considered to be blocked.

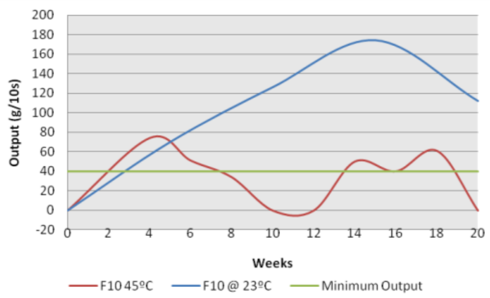

Figure 10. Foam dispensing test with F10 rubber formulation with α-PU foam.

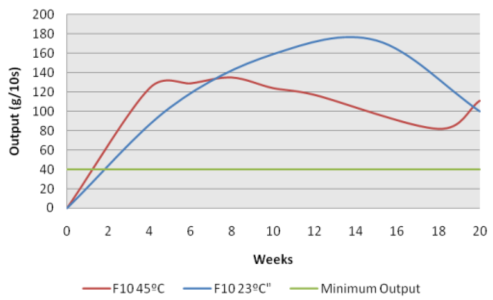

Figure 11. Foam dispensing test with F10 rubber formulation with β-PU foam.

Since that the F8 grommet was considered to have the best properties simultaneously with F10, its sticking and stucking test is being studied – figure 12. We can observe that we obtained results until the end of the test at 45ºC aging temperature, considering that we had an output higher than 40 grams per 10 seconds until week 22 – week 12 was the exception. As expected, comparing with the test performed at 45ºC, at 23ºC the quantity of foam dispensed is higher and the opening force of the valve smaller.

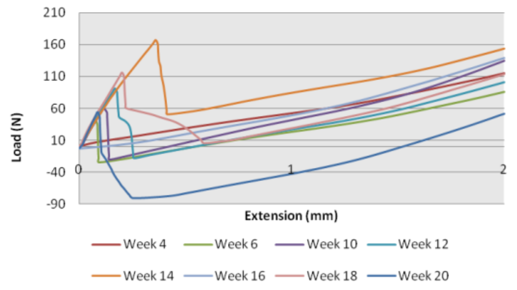

Figure 12. Opening load results at 45ºC with F8, using α-PU foam.

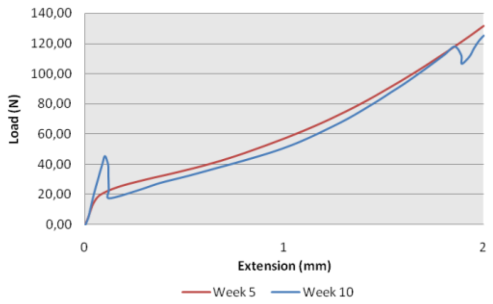

Figure 13. Opening load results at 23ºC with F8, using α-PU foam.

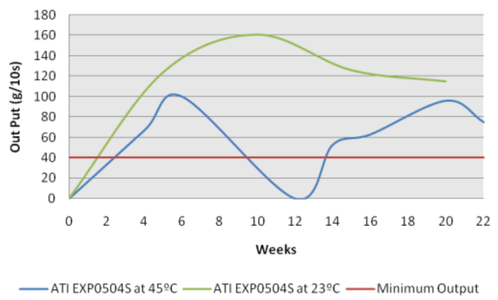

Figure 14. Foam dispensing test with F8 rubber formulation with α-PU foam.

3.3. Swelling studies

Swelling test was only performed on the best grommet chosen. The chemical behavior of these compounds with the chemicals used in PU aerosol cans, will determine the viability of the elastomeric material. The results below correspond to swelling after seven days immersing and after three drying days (figures 15-20).

When in contact with acetone, the samples generally swell, increasing its weight and volume, in which F10 samples are not in concordance (losing weight and volume). After 3 days drying, it was observed that all the samples suffered weight loss and the volume decreased, when swelled in acetone. The hardness of all the samples decreased after those 7 days of swelling and increased in contact with the air, after 3 days drying. The rubber material who suffered more variations of weight, volume and hardness was the F10 rubber sample.

The swelling test performed with the blowing gases showed that the variations on weight, volume are mostly negative or almost zero. The hardness increases after 7 and the 3 days drying, but the variation is smaller when compared with acetone or MDI.

The effect of the MDI in the samples is higher than the other swelling agents used. The fact is that the MDI is absorbed by the grommet, increasing its volume and weight after 7 days of swelling and, when in contact with air humidity, the rubber turns harder, having increases of 24,68% in the case of the F10 samples.

The samples supplied by B, F10 rubber samples, were the ones with the worst swelling behaviour.

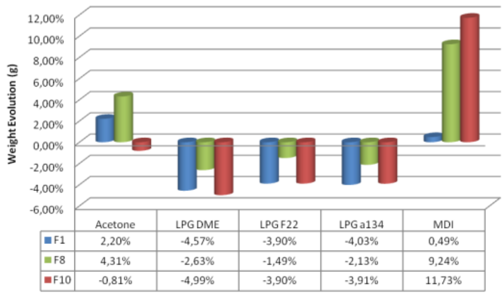

Figure 15. Weight evolution after seven days immersed.

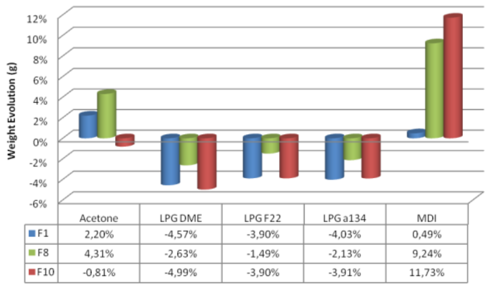

Figure 16. Weight evolution after seven days of immersion and three days drying.

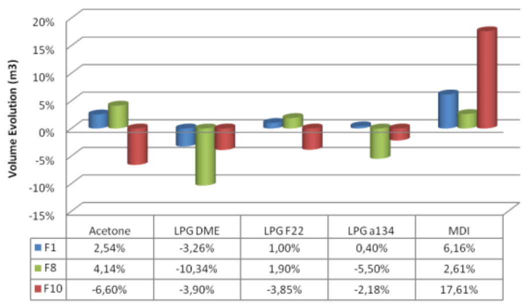

Figure 17. Volume evolution after seven days immersed.

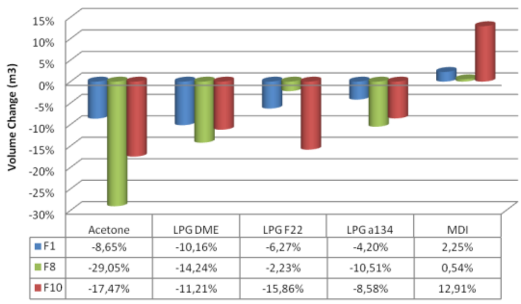

Figure 18. Volume evolution after seven days of immersion and three days drying.

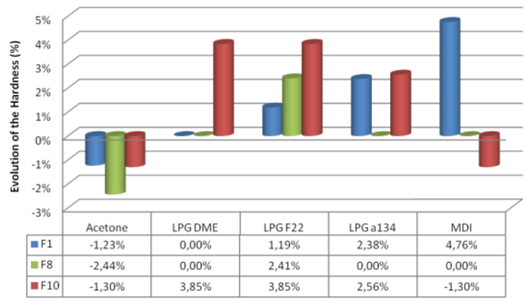

Figure 19. Hardness evolution after seven days immersed.

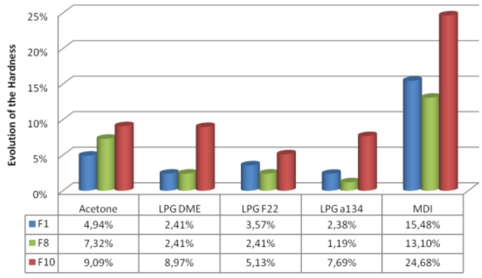

Figure 20. Hardness evolution after seven days of immersion and three days drying.

4. Conclusions

The improvement of chloroprene properties was achieved since the gases permeability and shelf-life of the new rubber formulations a better behavior when in comparison with F1 or F2.

Variables like additive quantities and qualities, cross-linking degree, plasticizer, that ATI manipulated during this period, influence rubber's boundary properties. It is known that the impermeability of a rubber is strongly dependent of the free volume existent in the rubber matrix. Adding carbon black, for example, will increase rubber mechanical resistance and, at the same time, it will fill the so common amorphous matrix of rubber materials, making gas diffusion trough the grommet more difficult. Increasing cross-linking degree will make the matrix less flexible, reducing the mobility of the chains, therefore reducing gases permeability, because the matrix has lower flexibility to allow gases to pass through it. A rubber with some cristalinity will improve the rubber impermeability too. For example, some additives like plasticizers can be soluble in certain compounds, changing completely the rubber quality. The fillers varies from supplier to supplier and different qualities of the same filler are used (suppliers are supplied also).

References

[1] Mark, Herman F.; Encyclopedia of Polymer Science and Technology Vol. 11 – Plastics Processing to Solid-state Extrusion, 3rd Edition; Wiley-Interscience, John Wiley & Sons, Inc. Publication, 2004

[2] Crawford, R.J.; Plastics Engineering, Department of Mechanical, Aeronautical and Manufacturing Engineering; Butterworth Heinemann, Third Edition, 1998

[3] www.2dupont.com