



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

Maria Luís Vieira Rodrigues

Dissertação para obtenção do Grau de Mestre em
Engenharia de Materiais

Júri

Presidente: Professora Doutora Fernanda Maria Ramos da Cruz Margarido,
Departamento de Engenharia de Materiais (DEMAT)

Orientação: Professor Doutor António José Boavida Correia Diogo,
Departamento de Engenharia de Materiais (DEMAT)

Professor Doutor João Carlos Moura Bordado, Departamento de
Engenharia Química e Biológica (DEQB)

Vogais: Doutor Eng. Aster de Schrijver, Altachem, Bélgica

Professor Doutor José Manuel Gaspar Martinho, Departamento de
Engenharia Química e Biológica (DEQB)

Outubro de 2009

I. Acknowledgments

A thesis is an academic work which is intended to evaluate the author. For me, this thesis was more than that. It made it possible for me to discover the attractive world of polymers and increase my knowledge in the scientific field. Moreover, it gave me the opportunity to meet interesting people with related interests and to live in a different and beautiful country.

For all this, a word of thankful gratitude is due to the following people:

- To my Professors, Antonio Correia Diogo and João Moura Bordado, who showed me this opportunity in this field and who, in spite of being physically absent there, were always there available to hear me, giving the best advices.
- To Mr Aster de Schrijver, for giving me the opportunity to learn “hands on job” inside his company and for providing the trainees with good conditions, essential to their well-being in the company and in Belgium.
- To Jordi Demey, for his helpful guidance, friendship and support. For his patience and good mood, and for trying to instill his knowledge the best way he could.
- To the staff of Altachem, for helping me whenever necessary.
- To my companions in Altachem- Sandra, Vitor, Andreia, Duarte, João, Ana’s, Inês, for for helping me and for being more than my colleagues, for being my friends. Also, to Antony, Ana Rafael, Joana Lobo, Andreia Ferreira, Miguel Correia, José Rodrigues, Filipa Luz, Ricardo Abrantes, a word of thankfulness for giving me his shoulder during these months.
- To all my friends that were worried about me, that called me, visited me and that made the distance a small detail.

My last thanks are for my parents, grandmother, brother and sister, uncles, for having always the right words and advice to help me and for not letting me forget what I am capable of.

II. Resumo

Este projecto baseia-se na investigação e no desenvolvimento de válvulas de aerossóis para espuma de poliuretano, focando-se no estudo do comportamento do anel de borracha (grommet), que permite a activação da válvula. Para responder às propriedades químicas e mecânicas do anel, foi necessário estudar novos compostos e encontrar novas soluções para as válvulas, resultando em dois subprojectos: melhoria das válvulas padrão da Altachem e desenvolvimento de uma nova geração de válvulas com maior vida útil.

A vida útil destes sistemas é dependente da impermeabilidade da borracha à água e aos gases usados nestes sistemas. A existência de água no interior destes sistemas promove a sua reacção com os grupos NCO livres do sistema, resultando na formação de um composto endurecido, poliureia. Esta reacção leva ao aparecimento de uma camada dura em torno da válvula e em regiões preferenciais do anel (regiões sob tensão de corte), que dificulta ou impede a abertura da válvula.

Foi testada a resistência química dos vários tipos de borracha dos diversos fornecedores. As perdas de gás, em recipientes com e sem espuma, foram seguidas e outros testes efectuados. Em particular, é imperativo o estudo do número de semanas após as quais a válvula continua a abrir, libertando espuma. Após a análise dos diferentes materiais, observou-se que a alteração dos materiais de enchimento, assim como a sua quantidade, na composição da borracha, altera a sua impermeabilidade e resistência química. O Neopreno® demonstrou ser a melhor escolha para aplicações em espumas poliuretanos.

Palavras-chave: Válvula de Aerossol, Anel de Borracha, Espuma de Poliuretano, Neopreno®, Elastómeros.

III. Abstract

This project is based on the research and development of aerosol valves to dispense polyurethane 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 Altachem 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 sticking 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®.

IV. About Altachem NV

Altachem NV is located in Deinze, a municipality in the Belgian province of East Flanders.

Established since 1992, Altachem is acting mainly in the market of 1, 1 ½ and 2 components polyurethane foams in aerosol cans, being the one-component foam (OCF) the most developed market amongst the referred ones.

Over the years, this company has invested a lot of time in developing and producing aerosol can valves, foam applicators and Foam Controlling Additives (FCA) for the foam industry.

This company tends to innovate and the R&D department is therefore a crucial element in Altachem NV. All the studies done and the current projects give an exclusive and distinctive knowledge in OCF that can be applied to foam applicator.

Since the one-component foam market keeps expanding, testing procedures and benchmarking methods are needed and gaining more relevance over the years.

Therefore, Altachem NV is looking for partnerships worldwide in the field of building chemicals and in particular on OCF.

IV. Table of Contents

1. Introduction to Polyurethanes	7
2. Aerosol Valves	10
3. Grommet Materials	15
4. Tests Performed	19
5. Experimental Results and Discussion	19
6. Conclusions and Future Work Perspectives	19
7. References	19

V. List of abbreviations

134a	Freon 134
ABS	Acrylonitrile Butadiene Styrene
CH	Can Horizontal
CCOH	Cycling Can On Head
COH	Can On Head
CV	Can Vertical
DME	Dimethyl Ether
DOT	Department of Transportation
EDPM	Ethylene Propylene Diene Monomer
F22	Freon 22
FKM	Fluoroelastomers
HG	Hard Grommet
LPG	Liquefied Petroleum Gases
MDI	Methylene Diphenyl Diisocyanate
NBR	Nitrile Rubber
NBS	Non-blocking System
OCF	One Component Foam
OP	Output Test
PE	Polyethylene
PP	Polypropylene
PU	Polyurethane
PVC	Poly Vinyl Chloride
RH	Relative Humidity
SG	Soft Grommet
SIR	Silicone Rubber
SS	Sticking & sticking
TPE	Thermoplastic Elastomers
TPP	Thermoplastic Polyesters
TPV	Thermoplastic Vulcanizates
TPU	Thermoplastic Urethanes

1. Introduction to Polyurethanes

Although the present study is mainly about research and development of aerosol valves, studying the rubber material behaviour, polyurethane foams were always present in all projects. Studying aerosol valves to dispense polyurethane foams imply its simulation in a real environment.

1.1. One Component Polyurethane Foam

Developed by Otto Bayer and his group of scientists in 1937, polyurethane (PU) foam was synthesized by the polymerization reaction between diisocyanate and diol. Over the years PU foam turned out to be a successful story as a business of many billion dollars. PU is a generic term, which refers to the repeating unit of NH-CO-O- , resulting from the reaction of isocyanate functionality with hydroxyl groups [1, 2].

One-component foams (OCF) were invented in UK within Imperial Chemical Industries in 1969 and, since that time, they have been used in several different applications. It contains a pre-reacted mixture of polyol, isocyanate, blowing agents and additives. Polyol is a macromolecule of polyhydric alcohols with molecular weights ranging from 200 – 8000 with functionalities ranging from 2 and 8. The -OH group of the polyol, in the presence of suitable catalysts, reacts with the -NCO radical of the isocyanate forming a urethane linkage (-NC). The catalysts accelerate the reaction to the required level and the blowing agent inflates the cells, increasing its volume and forming the light weight PU foam. The surfactants promote and stabilize the polyurethane cells and help retaining its shape into which it has been blown [1, 3].

Because OCF foams are supplied in pressurized vessels (like cans or cylinders), they are also called aerosol foams. Due to the gas pressure inside the container, the material inside is self-dispensed. While dispensing the mixture from its pressurized vessel, it expands to form a sticky froth that will adhere to the majority of surfaces. This froth reacts with atmospheric moisture expanding to the final form cured foam [3].

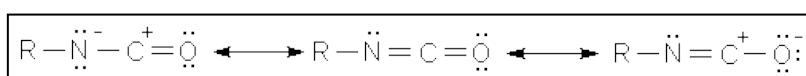
In general, to guarantee minimum acceptable foam properties in building applications, it is important that the foam presents good adhesion and elasticity, a certain resistance when compressed, dimensional stability and a certain yield per can. The minimum required physical properties should be independent from the room temperature, can temperature and from the age of the can [3].

Most PU are useful because of their physical properties and the breadth of applications is remarkable. They can be stiff enough to be used as structural members and soft enough for cosmetic applicator sponges. They can be used as the wheels of inline skates or cushions for furniture. It could be soft and flexible with entirely open cells, used as sealants for doors and windows frames, filling gaps around pipes (pipe insulation), coatings and adhesives. With other structures, PU foam can be used as thermoplastic elastomers (TPE) and fibres. In these

applications and hundreds of others, the chemistry can be summed up as a combination of hard segments and soft segments with varying degrees of cross-linking. This combination is, indeed, the strength of the chemistry [3, 4].

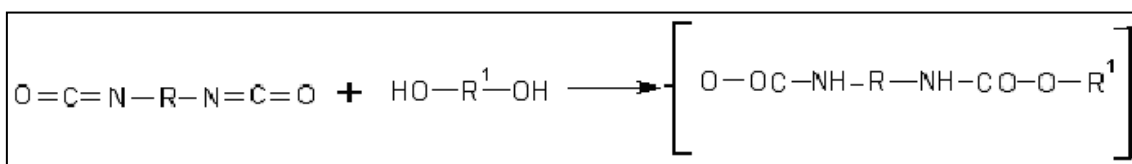
1.2. Polyurethane Chemistry

The reactivity of NCO is determined by its resonances - Scheme 1. However in the polyurethane technology there are other four main reactions in which the isocyanates are involved. The most relevant reactions where isocyanates are involved are the reaction with polyol to form polyurethanes (Scheme 2) and with water to form polyurea, releasing CO₂ (Scheme 3). Besides these reactions, isocyanate groups can also react with urethane and urea [2, 3].

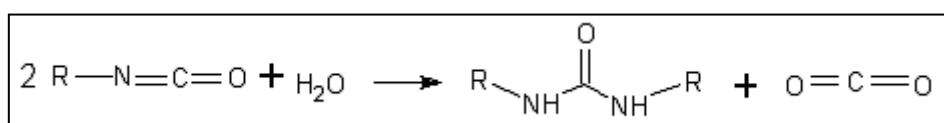


Scheme 1. Illustration of the three resonance structures of the isocyanate group.

Commercial polyurethanes are typically obtained by the reaction of a diisocyanate with a molecule containing at least two active hydrogens [2, 3].



Scheme 2. Reaction of polyaddition between polyol and isocyanate to form polyurethane.



Scheme 3. Reaction between isocyanate and water forming urea.

Even though these reactions occur to a much less extent than the primary reactions, their importance should not be underestimated [2, 3].

The foaming can be conducted through two different ways. In the first way, two component PU foam, isocyanate is added to the mixture while dispensing. The foaming will be carried out, for example with a physical blowing agent; the reaction between isocyanate and polyol produces

polyurethane linkages with the emission of heat of reaction. The blowing agent vaporizes; the gas is trapped in the closed cells of the foam [2, 3].

In the OCF foaming process, at the first stage an aerosol can is filled off with a mixture of a polyol blend, isocyanate, different additives and physical blowing agent like Liquefied Petroleum Gases (LPG) and Dimethyl Ether (DME). The prepolymerization reaction occurs inside the can: the polyol reacts with isocyanate which is present in excess [2, 3].

At the second stage, while dispensing, the liquid prepolymer leaves the can and starts to expand to low density froth by vaporization of the physical blowing agent. In this interaction between the polymerization and blowing reactions which take place simultaneously during foam formation, the heat given out from the polymerization reaction under adiabatic cure conditions enhances the blow reaction (i.e., the rate at which CO_2 is involved) [2, 3, 5].

Polyurea can form hard segments of flexible PU foams, with strong secondary bonds (hydrogen bonds) with a tendency to form hard segment domains. The blow reaction not only helps in foam expansion, but also leads to the generation of urea hard segments [6].

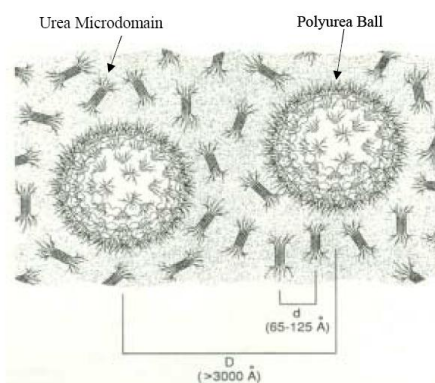


Figure 1. Schematic representation of the phase separation behaviour in polyurethane foams [6]

In addition, at higher water contents (and thus at higher hard segment contents), the urea micro domains are known to aggregate and form larger urea rich structures commonly termed “urea balls” or “urea aggregates”. The isocyanate-water reaction proceeds faster when compared to the reaction between the isocyanate and the polyol. This leads to the formation of oligomeric polyurea species which are termed as “urea hard segments” [6- 8]

The glycol most commonly used is the polypropylene glycol, which is obtained through anionic polymerization of propylene oxide, propylene and ethylene oxides copolymerization. Changes in a limited number of component parts allow a wide variety of products to be made. The foams used in this project are two standard foams, designated by 4230 and 3733, with different raw materials and quantities. The standard products used by Altachem to produce the standard

foams are described on table 1. The common formulation table used to make one can of each formulation is represented in Annex 2.

Raw Materials		Formulation	
		4230	3733
Polyol		GP1000 ¹	GP1000 and VD1000 ²
Extender		FCA100 ³	FCA100
MDI		Methylene Diphenyl Diisocyanate	Methylene Diphenyl Diisocyanate
Additives	Surfactant	-	Saxol 8002 or Struksilon 8002
		Tegostab B8871	
	Frame Retarders	Cereclor S45 ⁴	Cereclor S45
		TCP ⁵	TCP
	Catalyst	DMDEE ⁶	Niax A1 ⁷
DMDEE			
Blowing Agents	LPG	75%	45%
	DME	25%	55%

Table 1. Raw materials used produce one component polyurethane foams.

2. Aerosol Valves

The essential element in every aerosol dispenser is the valve. The valve can be a gun valve (picture 1, A) or a tilting one (picture 1, B), being the first activated by a gun for aerosol cans and the second one activated by an applicator. When actuated, the valve releases the product from confinement. It may deliver a very fine mist, a coarse spray, a very long beat, foam, or even a viscous gel or paste [9].

¹ Polypropylene Triol – Voranol CP 1055

² Polypropylene Diol – Voranol P 1010

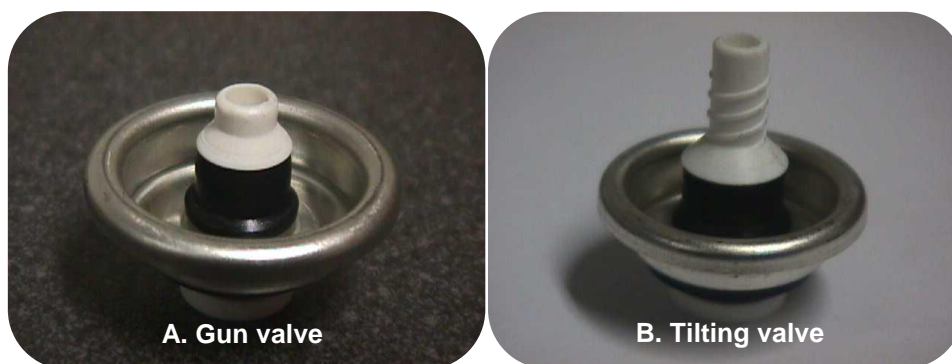
³ 1,2-Propylene Glycol or Propane-1,2-diol

⁴ Chlorinated Paraffin

⁵ Trichloropropylphosphate

⁶ 2,2 – Dimorpholinodiethylether

⁷ 70% bis-(2-dimethylaminoethyl-)ether and 30% dipropylene



Picture 1. Examples of gun and tilting valves.

The valve is also crucial, as well as the foam, gun and adaptor, to obtain good results when using OCF. The various valve components used in tilting and vertical valves for OCF must meet a large number of criteria set by each OCF manufacturer:

- Chemical resistance to different blowing agents and polyurethane chemicals;
- Shelf-life guaranty of 15 months, when stored vertically at different temperatures;
- Different ways of applying the foam (adapters + guns).

A typical aerosol valve is made up from 4 components, like this example described on figure 2:

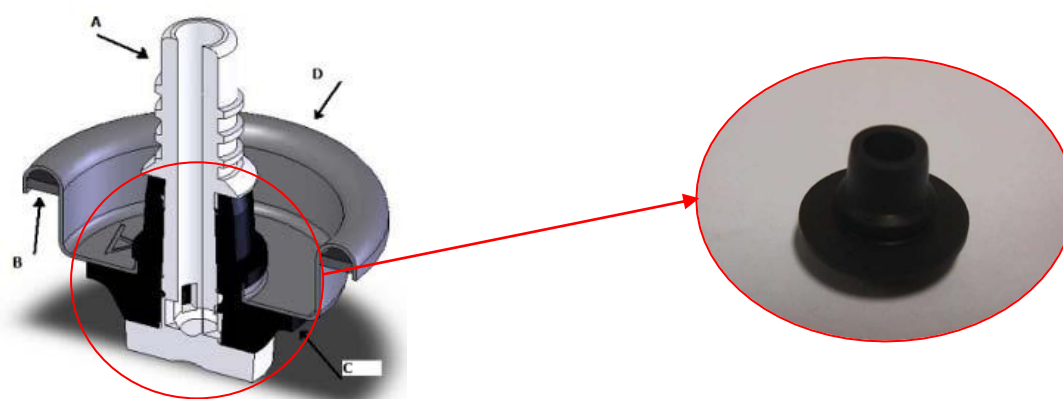


Figure 2. Aerosol valve (left) and grommet (right).

- Valve stem, which has orifices inside to allow the dispensing of the foam, made of polymer material.
- Inlayed gasket, which is the seal between the valve cup and the aerosol can, made of rubber.
- Grommet, usually made from vulcanized rubber.
- Cup, generally made of tin plated material.

Some stems contain three or even four orifices, depending on the nature of the product to be dispensed (higher or lower output). In the closed position the orifices are covered by the grommet, so the valve is closed, entrapping the foam and gas inside the can.

When the actuator is pressed, it pushes the valve stem through the soft grommet and the orifices are uncovered, allowing the foam to pass through the valve and into the applicator. When the pressure is released by the operator, the stem is pushed upwards due to the force applied by the grommet, covering the orifices [9].

The applicators are a very important tool to open tilting and gun valves. It can be a simple adapter with straw screwed on the tilting valves or, for gun valves, a NBS foam gun – examples can be observed in picture 2.



Picture 2. Applicator systems.

These systems reduce the valve opening forces and control the output (OP).


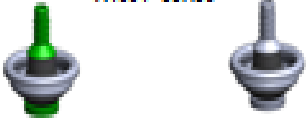



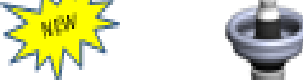
2.1. Valves Generations

We have four generations valves:

- Generation 1 – Valves A2000 and A3000;
- Generation 2 – Valves A3004 and A4004, with a better shelf-life;
- Generation 3 – Valves A3105 and A4105, with the best shelf-life;
- Non sticking valve – A5000 valve.

The series A2000, A4004 and A4105 are tilting valves and the series A3000, A3004 and A3105 are gun valves.

The last generation, generation 3, is the best generation of valves allowing the best shelf-life of all valves, allowing high efficiency and less sticking of the valve. On figure 3 is represented the three valves generations.

	Generation I	Generation II	Generation III
A D A P T E R	A2000-A4000 Series 	A4004 Series 	A4105 Series 
G U N	A3000 Series 	A3004 Series 	A3105 Series 
C H A R A C T E R I S T I C S	Standard Tilting Valve (A2000, A4000) & Gun Valves (A3000) Daily proven technology by Altechem Valve: High Modulus Polyethylene & Vulcanized Rubber Shore M70 Mounting Cup: tinplated 0.4 mm	Less Sliding Robust Tilting (A4004) & Gun Valve (A3004) Up to 5 x less sliding Valve: Special Copolymer & Rubber Material Mounting Cup: tinplated 0.4 mm	Less Sliding Robust Tilting (A4105) & Gun Valves (A3105) Designed for use in warm & humid climates Valve: Unique Rubber and Stem materials for maximum security and efficiency Mounting Cup: tinplated 0.4 mm


Increasing shelf life of the valves 

Figure 3. Altechem valves generations.

The A5000 valve is a different valve, with a higher performance than other generations, with a special grommet design and material. The grommet consists of two different parts – the upper softer polymer part, and a hard bottom part, shown on figure 4.

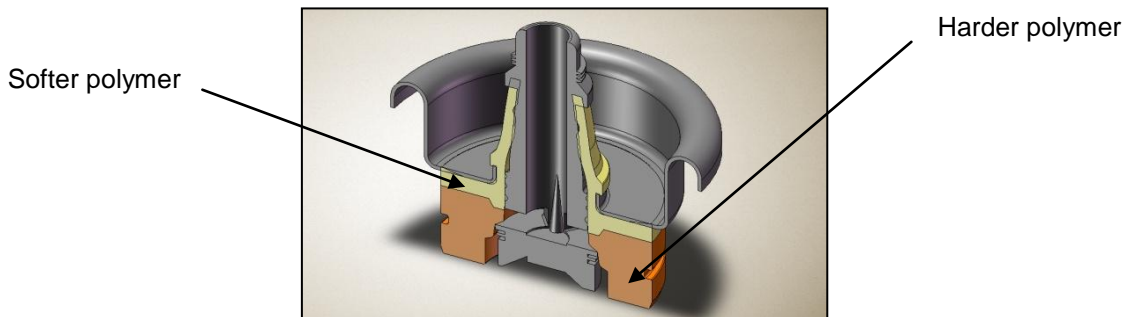


Figure 4. A5000 non sticking valve generation.

The softer part is made of a thermoplastic elastomer material (TPE), and the hard part of polymer material. These two components become only one by dual injection molding, with plasma treatment on the hard part after injection, to promote the adhesion between those two polymer materials.

The stem and its design are still important due to its sealing function, not allowing the foam to abandon the can without any kind of activity and avoiding that the foam can penetrate between the stem and grommet. The design of the standard and A5000 valves can be seen in annex 2.

2.2. Gun Valves

Gun valves belong to the vertical activation valves, like the A3000, A3004, A3105, A5000 valves.

This valve is used adapting it to a Non-blocking System (NBS) foam gun, where a vertical force applied into the stem will activate the valve (figure 5). When the gun is pressed it pushes the valve stem through the grommet and the orifices are uncovered, allowing the foam to pass through the valve and into the gun.

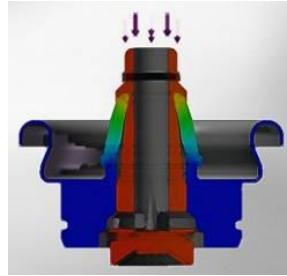


Figure 5. Gun valve opening force.

2.3. Tilting Valves

This valve is designated by “tilting valve” as a result of the lateral opening force applied in the stem to activate the valve, as shown in the figure 6.



Figure 6. Tilting valve opening force.

The tilting valves used in this project are A2000, A4004 and A4105 valves. When the valve is built the adapter or actuator may be fitted. When the actuator is pressed it pushes the valve stem through the grommet, and half of the orifices are uncovered, allowing liquid to pass through the valve and into the adapter [10].

3. Grommet Materials

In this project, the aim is to search and study thermoplastic materials to be used in the grommet, to reduce the gas losses, increase the shelf-life by reducing sticking & sticking behavior, 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.

This project is divided by two important developments: the development of the standard valve, with a lower cost and complexity; the development of a new generation valve, with higher production cost and higher complexity, but with higher impermeability, better chemical resistance and with a longer shelf-life, with a non-sticking behavior. The types of polymer materials studied and already in study for A5000 valves are thermoplastic elastomers (TPE's), which are different from the conventional synthetic elastomers used in the standard valve.

The important question then arises: How do we decide which polymer is the best for this particular application? Material selection is not as difficult as it might appear but it does require an awareness of the general behavior of polymers as a group, as well as a familiarity with the special characteristics of individual polymer.

The first and most important step in the design process is to define clearly the purpose and function of the proposed product and to identify the service environment. Then one has to assess the suitability of a range of candidate materials. The following are generally regarded as the most important characteristics requiring consideration for most engineering components [11].

- (1) Mechanical properties - strength, stiffness, specific strength and stiffness, fatigue and toughness, and the influence of high or low temperatures on these properties;
- (2) Corrosion susceptibility and degradation;
- (3) Wear resistance and frictional properties;
- (4) Special properties, as thermal, electrical, optical and magnetic properties;
- (5) Molding and/or other methods of fabrication;
- (6) Total costs attributable to the selected material and manufacturing route [11].

3.1. Rubber Compounding and Additives

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 [12].

Compounding is a term that has evolved within the polymers and rubber industry and, in many aspects, is an incongruity for the material science of modifying a polymer or polymer blend

through addition of other materials to achieve a set of mechanical, physical and chemical properties, for a specific application. On the other hand, it is a high complex science involving many traditional disciplines such as organic chemistry, polymer chemistry, materials physics, mathematics and engineering mechanics [12].

Raw materials for a compound are generally selected in the following order:

- Polymer (natural or synthetic rubber);
- Fillers or reinforcing agents;
- Antioxidants and antiozonants;
- Plasticizers or oils;
- Bonding agents or adhesives (if needed);
- Tackifier (if needed);
- Vulcanization system (curing agent, accelerator(s) or coagent) [12].

Fillers are particulate materials added to improve the physical properties and optimize the cost of the rubber compound. All particulate fillers increase the hardness and stiffness of rubber compounds. The chemical composition and its effect on rubber compound physical properties typically classify fillers into three broad categories: nonreinforcing, semireinforcing or extending and reinforcing fillers. The reinforcing fillers improve the physical properties of the rubber vulcanizate, while some fillers simply act as diluents or extenders [12].

3.1.1. Fillers

Some fillers, such as short fibers or flakes of inorganic materials, improve the mechanical properties of a plastic. Others, called extenders, permit a large volume of a plastic to be produced with relatively little actual resin. Calcium carbonate, silica and clay are frequently used extenders [11].

Carbon Black is the primary reinforcing filler used in the rubber industry. Primarily owes its reinforcing character to the size and shape of the aggregate structure (essentially spherical particles chemically bonded). The two most important properties of carbon black are surface area and structure. Surface activity is the strength of the carbon black/rubber interaction either from nonbonded physical interactions or chemisorption and the structure depends upon the size and agglomeration of the particles. Carbon black can be classified into reinforcing (increasing the tensile strength), semi-reinforcing and extender blacks. This filler is used as reinforcing filler in a variety of rubber products including consumer products such as automobile tires, footwear and shock absorbers, and industrial applications such as conveyor belts, dock fenders and roofing materials [12, 13].

Mineral fillers and synthetic fillers are naturally occurring materials that are mined and grounded to a specified particle size. Fillers like extender fillers and/or like calcium carbonate, kaolin clay (hydrated aluminum silicate), calcium silicate, zinc oxide, carbonates, silica and clay,

can reinforce the rubber by increasing the young modulus, tensile strength, the abrasion resistance. Talc is often used to provide smooth surfaces appearance and large platelets of talc provide a barrier to gases and moisture permeability in compounds [12].

- Precipitated calcium carbonate is used as semi-reinforcing filler particularly when resistance to alkali solutions is needed.
- Metal oxides like zinc and magnesium are used as reinforcing filler when heat resistance is required but in the last several decades is used as activator for the sulfur cure system or as curatives for chloroprene rubber compounds.
- Silicates like aluminosilicates with mixed Al_2O_3 and SiO_2 , magnesium aluminosilicates and calcium silicates are the most important types and can be used as reinforcement.
- Silica, because of its small particle size and complex aggregate structure, precipitated silica imparts the highest degree of reinforcement to rubber among all of the nonblack particulate fillers. This filler is used too to improve chunking and tear resistance, resistance to wear, tearing, flex fatigue and heat aging [12, 13].

Most polymers, because they are organic materials, are flammable. Therefore, is imperative to add flame retardants to reduce the probability of combustion, like **chlorine**, **bromine**, **phosphorous** or **metallic** salts [12].

3.1.2. Antidegradants

Good aging properties of rubber compounds are essential to provide required service life of rubber products. The type of elastomer used is the principal factor considering aging properties. In general, the more saturated the backbone of the elastomer, the better are its aging properties. Unsaturated polymers are susceptible to thermal oxidation or to ozone. Thus, antioxidants and antiozonants are needed to extend the useful service lives of products made with these elastomers [12].

Stabilizers prevent deterioration of the polymer due to environmental factors. Antioxidants are added to ABS, polyethylene and polystyrene, for example. Heat stabilizers are required in processing polyvinyl chloride. Stabilizers also prevent deterioration due to ultra-violet radiation [11].

The antioxidants commercially available may be divided into three classes: secondary amines, phenolics and phosphites. Many antioxidants in these classes are volatile at elevated temperatures and almost all are readily extracted from the vulcanizates by the proper solvent. As a result, to provide an increased protection against oxidation under severe temperature and solvent extraction conditions, the use of polymer-bond antioxidants is included. Therefore, the chemical bonds between the antioxidant and the backbone will eliminate the volatility and extraction of the antioxidant [12].

3.1.3. Plasticizers

Plasticizers are low molecular weight materials which modify the properties and forming characteristics of the plastic. An important example is the production of flexible grades of polyvinyl chloride by the use of plasticizers [11].

To improve processing and to plasticize the rubber compound is commonly used petroleum, ester or stearic acid [12].

Petroleum plasticizers are the most universally used plasticizer for all rubber compounds. They improve the flow and processing properties and also reduce the final cost of the compound. Aromatic process oils are the most common plasticizer for general purpose rubbers. Naphthenic and paraffinic process oils can be used too [12].

Ester plasticizers are used in high polar elastomers, such as Neoprene® and nitrile rubber, to improve low and high temperature performance or impart particular oil or solvent resistance to a compound. Resins and tars are added to impart tack, soften the compound, improve flow and in some cases to improve the filler dispersion [12].

Stearic acid is used in many compounds as a cure activator and in addition may act as a processing agent. Thus, stearic acid may be the most widely used processing agent in the rubber industry [12].

3.1.4. Vulcanization System

Vulcanization is a chemical process where sulfur or other materials form crosslinks in the elastomer and thereby improve the polymer's mechanical properties. In many instances, not all of the desired properties reach an optimum level simultaneously. The task is to achieve a balance of the most important property requirements through design of the cure system and time-temperature cure cycle, to attain the necessary compound mechanical properties [12].

Sulfur is the most common vulcanizing agent for rubbers such as SBR and polybutadiene. Because of its insolubility in water, it resists to migration to the surface prior to cure, originating a better building tack and better component-to-component adhesion [12].

Peroxides are probably the most common materials used after the sulfur because of their ability to crosslink a variety of elastomers and to produce thermally stable carbon-carbon crosslinks. The carbon-carbon bonds are inherently stronger than the carbon-sulfur bonds. Peroxides when heated decompose producing active free radicals, which in turn react with the rubber to produce crosslinks [12].

Halogen-containing elastomers such as polychloroprene and chlorosulfonated polyethylene are crosslinked by their reaction with metal oxides, typically zinc oxide. The metal oxides react with halogen groups in the polymer to produce an active intermediate which then reacts further to

produce carbon-carbon bonds. The zinc chloride is liberated as a by-product and acts like an autocatalyst [12].

Other examples of bifunctional compounds used for curing are epoxy resins for nitrile rubber, quinine dioximes for butyl rubber and phenolic resins for EDPM (and some TPEs) [12].

The carbon linkages gives excellent thermal stability and permanent set resistance, often approaching those of peroxide curing [12].

3.2. Thermoplastic Elastomers

See annex 8.1.

3.3. Properties of Thermoplastic Elastomers

See annex 8.2.

4. Tests Performed

See annex 8.3.

5. Experimental Results and Discussion

See annex 8.4.

6. Conclusions and Future Work Perspectives

See annex 8.5.

7. References

See annex 8.6.