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Development of Different ECOFAST FOAM (Ecological Fast Curing Foams) Formulations

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II. Resumo

A estrutura química das espumas de poliuretanos de um e dois componentes, utilizada em latas de aerossol, não sofreu qualquer tipo de alteração nos últimos trinta anos. Sendo um poliuretano produzido por reacção de isocianatos com poliois, a toxicidade dos produtos relacionados com a indústria de poliuretanos é um problema grave. Não só os isocianatos são produtos tóxicos, como alguns dos aditivos utilizados são igualmente tóxicos, como por exemplo a parafina clorada.

Com vista a substituir estes materiais tóxicos, tinha-se como objectivo desenvolver uma alternativa que substituísse as resinas tóxicas por produtos amigos do ambiente. Estas resinas amigas do ambiente baseiam-se em resinas acrílicas. Se à resina acrílica for necessário juntar um plastificante na rede estrutural, utilizam-se ácidos gordos saturados e insaturados em detrimento dos materiais clorados. O desenvolvimento elaborado em espumas ecológicas de um e dois componentes visa tornar estas espumas um produto comercializável e para tal estas novas espumas necessitam de certificação e classificação em resistência ao fogo.

O uso de espumas acrílicas é benéfico também do ponto de vista do tempo de cura e expansão da espuma. Enquanto as espumas de PUR expandem durante a cura (processo que pode ocorrer até 12 horas), a cura por radicais em resinas acrílicas é tipicamente bastante mais rápida. A expansão após o spray deixa de ser observada, pois a estrutura e reactividade destas resinas não se baseia na reacção com a água presente no ar.

A procura e síntese de novas estruturas químicas irão levar ao desenvolvimento de espumas ecológicas que conseguirão substituir as espumas de PUR nas suas diferentes aplicações: preenchimento e isolamento de fendas, fixação e isolamento de portas e janelas, isolamento de superfícies, etc.

O desenvolvimento da composição das espumas em estudo depende de vários aspectos, uma combinação adequada de inibidores e aceleradores de modo a produzir uma espuma que cure no menor tempo possível e cujo sistema de dispensa não sofra bloqueio. Uma compatibilidade com diferentes gases, gases liquefeitos, CO_2 e outros. E outras características como viscosidade, densidade, tenacidade, flexibilidade na compressão, resistência à tracção também são aspectos relevantes na investigação.

A utilização de um mecanismo de reacção iniciado por radicais implica o uso de um inibidor, que não pode ser adicionado à resina antes do início da reacção de polimerização. Esta condição foi necessária aos presentes resultados num sistema de dois componentes: um componente sendo a resina e o outro componente o inibidor. Numa fase posterior de desenvolvimento, pretende obter-se uma forma de armazenar um inibidor na resina num estado não activo.

Palavras Chave: Projecto ECOFAST, Resina Acrílica, Polimerização, Acrilatos de uretano.

III. Abstract

Actually, the chemical backbone structure of one component and two component foams used in aerosol can has not been changed for the last thirty years; isocyanates react with a polyol mixture, rendering a polyurethane network. The toxicity of the products involved in the polyurethane foam business remains however a large problem, not only are the used isocyanates basically toxic products, also some of the used additives are toxic, e.g. chlorinated paraffin's.

To replace these current toxic chemicals, an alternative will be developed using non-toxic resins with the use of ecological friendly additives. The resin will be based on acrylic resins. If necessary, as plasticizer for the network, unsaturated or saturated fatty acids will be used, replacing nowadays chlorinated materials. The development of both one and two component foams is envisaged towards an actual commercial product possessing the needed certificates and flame retardancy classification.

The use of acrylic resins is also very beneficial towards the curing time and expansion of the foamed material. While PUR foams largely expand during curing, this can last up to 12 hours, the radical curing of acrylic resins is typically faster, an expansion after spraying is no longer observed since the structure and reactivity of these resins are not based on the reaction with water present in air.

The search and synthesis of new backbones will result in the development of foams, ready to replace the existing PUR foam compositions in their different application fields: filling and isolating gaps, fixation and isolation of doors and windows, isolation of surfaces, etc. The development of the foam compositions will depend on several aspects needed for the foam: a suited combination of initiators and accelerators needs to be investigated in order to produce a froth which can be cured in the smallest possible time, avoiding however blocking of the dispensing system. Compatibility with different possible blowing agents: liquefied blowing gases, CO_2, and others. Other characteristics like froth viscosity, density, toughness, compression flexibility, tensile strength and others need to be investigated.

The use of a radical initiated reaction mechanism implies the use of an initiator, which cannot be contained in direct contact with the resin without starting the crosslinking reaction. These results in an initially two component system: one part containing the resin, the other the initiator. In the development phase, a way to stock inhibited initiator in the resin can will be investigated

Keywords: Ecofast Project, Acrylic Resin, Crosslinking, Urethane Acrylates.

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 the valves and guns. Nevertheless, new ideas to incorporate health and environmentally friendly aspects based in new technologies are being developed. This includes the ECOFAST project.

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.

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UA – Urethane Acrylates

PUF – Polyurethane Foam

PUR – Polyurethane Resin

OCF – One Component Foam

TCF – Two Components Foam

BPO – Benzoyl Peroxide

UPEST/**UP** – Unsaturated Polyester

ATF – Acrylic Type Foams

UAO – Urethane Acrylate Oligomer

AFS – Alta Foam Scan

AFM – Alta Foam Monitor

TFMA – Trifunctional Methacrylate

MFMA – Monofunctional Methacrylate

BFMA – Bi-functional Methacrylate

1 Introduction

To start knowing which behavior and what properties we should expect and/or improve in the urethane acrylics (**UA**'s), it's important to start our study by focus on Polyurethane Foams (**PUF**'s) since they will serve as our reference. Some PUF's were studied in order to understand which properties are more important for the purposes of the various types of foam (flexible, semi-rigid and rigid).

1.1 Polyurethane History (1)

The pioneering work on polyurethane polymers was conducted by Otto Bayer and his coworkers in 1937 at the laboratories in Leverkusen, Germany. They recognized that using the polyaddition principle to produce polyurethanes from liquid diisocyanates and liquid polyether or polyester diols seemed to point to special opportunities, especially when compared to already existing plastics that were made by polymerizing olefins, or by polycondensation.

Commercial production of flexible polyurethane foam began in 1954, based on toluene diisocyanate (TDI) and polyester polyols. The invention of these foams (initially called imitation Swiss cheese by the inventors) was thanks to water accidentally introduced in the reaction mix. These materials were also used to produce rigid foams, gum rubber, and elastomers.

The first commercially available polyether polyol, poly (tetramethylene ether) glycol), was introduced by DuPont in 1956 by polymerizing tetrahydrofuran. Less expensive polyalkylene glycols were introduced by BASF and Dow Chemical the following year, 1957. These polyether polyols offered technical and commercial advantages such as low cost, ease of handling, and better hydrolytic stability; and quickly supplanted polyester polyols in the manufacture of polyurethane goods.

In 1960 with the availability of chlorofluoroalkane blowing agents, inexpensive polyether polyols, and methylene diphenyl diisocyanate (MDI) heralded the development and use of polyurethane rigid foams as high performance insulation materials. Rigid foams based on polymeric MDI (PMDI) offered better thermal stability and combustion characteristics than those based on TDI.

1.2 Polyurethane Foams

Cellular microstructures are widely used in both nature and by man to conserve material characteristics in combination with a reduction in weight of these materials and structures. One of the main uses of cellular microstructures nowadays is as space-filling structural foam (2). All classes of polymeric materials can be foamed and used for several purposes. For example, thermoplastic polymers like polyethylene, polypropylene, and also thermoplastic starches can foamed and used as packaging materials or constructional material (3) (4) (5) (6). Another major example is the foaming of thermosetting materials. Cross-linked polyurethane foams (PUF) are used widely for insulation in construction, transportation and industrial applications like refrigerators, freezers, cavity walls, floor panels, roofing materials (7). On the other hand PUF's have been used as filling and insulating material for the construction of houses and buildings for more than 30 years (8).

1.2.1 One Component Foam (OCF) and Two Component Foam (TCF)

Polyurethane foams can be divided into two major categories: one and two component foams (OCF and TCF, respectively). In two component foams, the polyol and isocyanates mixtures are stored in different pressurized containers or aerosol cans. Mixing is proceeded during the casting or spraying of the material, depending on the type of application (to produce sheets and foam blocks or to fill cavities). After spraying or casting, the isocyanates react with the polyol mixture; the heat of the reaction vaporizes the present physical blowing agent, creating a fine-mazed cell structure. Two component foams can vary from very rigid to softer, more elastic materials to be used in car seats and as building blocks (9) (10).

In one component foam applications both the isocyanates and polyols are mixed within one aerosol can with a known excess isocyanate. A polyurethane prepolymer is formed with cyanate end groups. Upon spraying, the sprayed prepolymer, i.e. froth, expands due to the evaporation of the physical blowing agent. The isocyanate end groups react with water present in air to form urea linkages and CO_2, a second expansion is observed. OCF usually are more elastic and serve mainly as filling materials; more rigid PUR foams can however also be obtained.

Properties	Typical Range
Density (ODM)	25 – 30 g/l
Adhesion Strength	80 – 150 kPa
Shear Strength	22 – 50 kPa
Compression strength at 10 %	33 – 120 kPa
Water absorption	0,3 % volume
Tack free time	15 min at 23 °C – 50 % RH
Yield per 100 ml	3,25 liters
Closed cells	60 – 70 %

Table 1 - Typical property range of one component PU foams

Properties	Filling Foam	Fixation Foam
Overall Density (g/l)	25,0	29,5
Maximum Adhesion To Wood (KPa)	80,0	145,0
Compression Strength at 10 % (kPa)	30,0	100,0
Maximum Shear Strength (kPa)	25,0	50,0
Dimensional Stability at 40°C/90%RH	Max 4,0 %	Max 2,0 %

Table 2 - Physical requirements for PU foams at 23/23 °C –50% RH

1.2.2 Polyurethane Foam Components

The desired end properties of the foam dictate the choice of specific components along with their required quantities. There are many different components needed to synthesize PU foam. The seven major ones are:

- **Polyols**

The polyol is needed to obtain a urethane prepolymers and the type of polyol defines the physical properties of the final foam. The lower the viscosity of the polyol the lower is the viscosity of the prepolymers for the same NCO value.

The polymer properties are met primarily by the degree of crosslinking, and this, in turn, is achieved by an appropriate choice of both molecular weight and functionality of the polyether (or polyester) resins used for coupling with the MDI.

Type of Polyol	Molecular Weight	Functionality
Glycerol	92	3
Ethylene diamine	60	4
Sorbitol	182	6
Sucrose	342	8

Table 3 - Type of Polyols

Flame Retardants

A semi rigid OCF is highly crosslinked and therefore less flammable than flexible foams. Two basic routes are possible to obtain urethane foams with reduced flammability:

- Altering the structure of the urethane molecule to produce an inherently flame retarded foam.
- Applying flame retardants in the foam on reactivities, additives or post-treatments of the foam.

TCPP or TCEP is a common used flame retardant. The flame retardant acts not only as a fire retardant but also as a plasticizer and helps making the prepolymers components more compatible.

Silicones

The stability of the cells of the froth is greatly influenced by the surface tension of the liquid. The greater the surface tension, the greater is the restraining force against expansion. The surface tension of a liquid depends on the surfactant, temperature and pressure of the expansion gas (which is dependent on temperature and gas volume generated).

Silicone depresses the surface tension of the polymer mix. Optimum stability is obtained when the surface tension reaches the lowest value. Not adding silicone causes froth collapse before the polymer reaches the curing point.

Catalysts

Catalysts cause thickening and a tendency for gelation on long standing. Cure times can vary from several hours with 1 pbw for 100pbw of Polyol down to about 15 minutes for tack free surface using 6 parts.

An excessive high level of catalyst will of course reduce the shelf life of the prepolymers but will also coarse foams.

The catalyst actually used in most OCF formulations today is DMDEE, this catalyst has the following advantages, no gelling activity, high blowing activity, high boiling point and no hydrolysis of the finished product.

MDI

The MDI is needed to form the urethane prepolymers. The purer the MDI, the less quantity is needed, the less are the side reactions in the prepolymers formation. The higher the NCO value of the prepolymers, the lower viscosity will be and the longer will be the shelf life of the prepolymers. Also an high NCO value will result in a poor texture and a poor froth stability of the cured foam.

Blowing Agents

The blowing agent is the most important additive because provides the pressure needed to drive the material out of the can. A high % of gas by volume can lead to a very big pressure. In this case, the gas will be lost while spraying and can occur sputtering.

The %gas also causes some changes in the overall density. A low % of gas will not permit that the material inside the can to be fully driven out.

The DME is used to increase the dissolution of all components. If a higher than the optimum % of DME is used, the resultant spraying process will be bad.

Chain Extenders

Chain extenders are low molecular weight polyols or polyamines, also referred as curing agents. Chain extenders are difunctional substances like glycols, diamines or hydroxylamines. These substances react with diisocyanates to form polyurethane or polyurea segments, in the urethane polymer(1).

Fillers

Fillers are used mainly with cost reduction objectives. They can sometimes confer to the foam some special properties, such as an increase of the compressive strength or flammability (flame retardants).

- **Plasticizers**

Plasticizers are non-reactive liquids such as phthalates, benzoates and chlorinated paraffin used to soften PU foam. Their use permits the reduction of both viscosity and costs. But in consequence, the physical properties of the foam are usually negatively affected (1).

1.3 Chemical Backbones – State of art

As we are looking for a new chemical backbone with a faster curing rate and more ecological beneficiary behavior, we are looking for different types of backbones. To fasten curing kinetics, we are in a first stage looking at radical polymerization of double bonds. For example, unsaturated polyesters, unsaturated biodiesels or more specific synthesized backbones can be envisaged.

1.3.1 Unsaturated Polyester Resins

From unsaturated polyester resins or UPEST resins, rigid foams are made mainly for construction purposes. Large containers filled with resin cast the curing material onto the desired substrates or production lines (11) (12) (13) (14). For these foams, the main focus is to lower the density of the foam versus a non-foamed cured UPEST resin. Below a description is given about the general principles of polyester foams as described by literature (15) (16) (17) (18) (19) (20) (21).
Generally, overall densities between 100 and 750 g/l are reported for this kind of foam. UPEST resins are made by the polycondensation of a mixture of saturated and non-saturated diacids and diols. The choice of the kind of diacids and diols depends on the level of stiffness that a producer wants to obtain for the cured material: phtalates import stiffness, aliphatic diacids promote flexibility (22). The amount of unsaturations present in the UPEST resin will determine the crosslink density. The UPEST resin is mixed with vinyl monomers, up to 30 to 40 weight% to control the viscosity of the non-cured resins. Again, the choice of these monomers will determine the thermo physical characteristics of the foams. Styrene monomers will import stiffness and alkenes will import flexibility.
The UPEST resin is usually cured by means of peroxide initiators like benzoyl peroxide (**BPO**), lauryl peroxide, dicumyl peroxide and others. Usually tertiary amines and organometallic compounds like diethylene aniline, ethoxylated p-toluidine, dimethylene aniline, Cobalt octoate, and others are used as accelerators for the initiation reaction of

the peroxides. Via this radical chain polymerization route, the double bonds of the UPEST and vinyl monomer are crosslinked. The radical initiator is usually added to the mixture directly before the casting of the resin onto the desired substrate, in one case the initiator resin was emulsified in water and separated from the initiator which was present in the water-rich phase (23).

There are several ways to blow the UPEST resin while curing. Both chemical as physical blowing agents are used. Physical blowing agents include mainly water and alkali blowing agents. In a single case acetone is mentioned (24). Chemical blowing agents include short chain amides and amines incorporated into the UPEST backbone, producing nitrogen containing gases due to the heating while curing like sulfonyl hydrazide (16) (17) (22). Another example is the use of carbonates, bicarbonates, perborates and perphosphates in combination with an acid source, producing gases due to their degradation upon heating (18) (15). In a single case, the use of a polyisocyanate was mentioned as a blowing agent when used in low quantities, reacting with water to form $C0_2$ and a urea linkage (19).

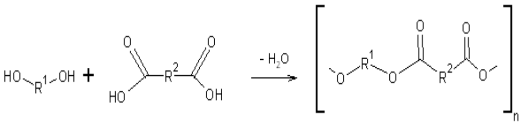


Figure 1 – Polycondensation of polyesters

In recent developments, both saturated and unsaturated polyesters are used in the PUR foam field. For example, fully saturated polyesters like PET are nowadays used as polyols in PUR foams (25). In this case, the actual chemistry of the PUR foam on itself is not altered; the only difference is an alteration in the starting material, e.g. a difunctional short chain PET-glycol instead of polypropylene glycol.

Another example is the combination of both PUR and UPEST foam strategies in two component systems (26) (27) (28) (29) (30). For example, can A contains the UPEST resin, polyol, additives and blowing agent; can B contains a polyisocyanate, peroxide and blowing agent. Upon mixing, both polyurethanes are formed together with a crosslinked UPEST resin, blown up in a very rigid foamed structure (31). Also, in a single case, the blowing of fully saturated polyesters is mentioned (32).

As more specific backbone structure, we will look at several double bond terminated molecules. Producers like Sartomer, Rahn, and others produce for the acrylate coating industry several different backbones like polyethylene glycol, polypropylene glycol, polyurethane and (saturated) polyester with different molecular weights, each time terminated with an acrylate double bond (33). This kind of acrylate terminated molecules can be used as the single molecule to construct a complete foam if this molecule possesses all characteristics needed for a foam. To investigate the possibility of making such a molecule, several different backbones will have to be produced with lab synthesis.

1.3.2 Urethane Acrylates

The chemistry of urethane acrylates is very versatile and there are four parameters that can be varied while synthesizing urethane acrylates:

- Functionality
- Type of isocyanates
- Type of polyol modifier
- Molecular weight

Functionality

For urethane acrylates, the functionality parameter varies in practice between one and six. Generally speaking, the lower the functionality, the lower is the reactivity, the better is the flexibility and the lower is the viscosity. Functionality two and three are good compromises for general-purpose oligomers.

Monofunctional urethane acrylates are used to improve adhesion to difficult substrates and improve flexibility (very low viscosity).

High functionality urethane acrylates are used to improve reactivity, scratch resistance and chemical resistance. Due to their high viscosity, these products are used at low levels in the formulation.

Types of Isocyanates

Essentially, four types of isocyanates are used for urethane acrylate synthesis: monoisocyanates, aliphatic diisocyanates, aromatic diisocyanates and polymeric isocyanates.

Monoisocyanates are used for monofunctional urethane acrylates only, while diisocyanate are used by far for most widely urethane acrylate synthesis. We can divide them in aliphatic and aromatic diisocyanates.

Aromatic diisocyanates

The aromatic diisocyanates are used for the manufacture of aromatic urethane acrylates. The incorporation of an aromatic diisocyanate makes the urethane acrylate harder and gives it a better scratch resistance. This aromatic urethane acrylates have also significantly lower cost than aliphatic urethane acrylate. The major drawback of the aromatic urethane acrylates is that they tend to yellow and therefore they are less appropriate for long lasting applications.

Aliphatic diisocyanates

The aliphatic diisocyanates are used in aliphatic urethane acrylates. Aliphatic urethane acrylates are slightly more flexible than aromatic urethane acrylates with the same functionality, a similar polyol modifier and at similar molecular weight. The main advantage of aliphatic urethane acrylates is the fact they can be used for long lasting applications.

The Polyol Modifier

The polyol modifier is the backbone of the urethane acrylate. Polyol modifiers vary in chemical type, functionality and molecular weight. Polyether urethane acrylates are typically more flexible than polyester urethane acrylates and often lower cost. They present slightly lower viscosity than a polyester urethane acrylate, with the same functionality and approximately the same molecular weight.

The functionality of the polyol modifier determines very often the functionality of the urethane acrylate and the molecular weight of this polyol modifier has big influence on properties like reactivity, viscosity and flexibility. General speaking, the higher the molecular weight of the polyol modifier, the higher is the flexibility, the lower the reactivity and the lower is the viscosity of the urethane acrylate.

The Molecular Weight

The molecular weight is mostly determinate by the polyol modifier for di- and trifunctional urethane acrylates. For higher functionality urethane acrylates this is not always the case and therefore the general guidelines for property/molecular weight correlation may be different.

1.3.3 Oligomers Route

The right choice of the oligomer is critical, normally the oligomer is the most important component in the formulation by weight. Because of this, its choice has a major impact on the final performance of the system. Some of these characteristics are reactivity, gloss, adhesion, chemical resistance, scratch resistance and abrasion resistance. In addition to this, cost is also an important selection criteria.

1.3.3.1 Urethane Acrylate Oligomers

Mostly urethane acrylate (methacrylate) oligomers (**UAO**) with different functionality, try to have the PU foams mechanical advantages. They bring specific favorable toughness to the foam, forming Urethane H – bond Net (>N –H ….O = C<) in parallel with the Acrylic crosslinking net during the cure. Having different functionality, they provide Urethane groups with different mobility in favor of smooth forming the Urethane – H bonds Net throughout the course of the cure. Additionally the formation of this net plays the role of natural regulator of the polymerization speed, preventing high jumps in the cure process temperature.

- **Disadvantages of UAO**:

- Increased viscosity when compared to other types Acrylic Oligomers with similar M_w.
- Tendency to Crystalline formation.

The rest parts of the acrylic monomers, with their versatility, are employed to play the role of efficiently selected active diluents for UAO in order to avoid above mentioned disadvantages:

- To reduce the viscosity of UAO;
- To prevent crystalline formation before spraying;
- To increase the gas solvency of the UAO;
- To improve the characteristics of the foams.

1.3.3.2 Unsaturated Polyester Oligomers

Unsaturated polymers include polyesters like polyethylene terephtalate and polyethers like polyethylene glycol. According to the present invention, preferably unsaturated polyester is used for the PU backbone. Any polymer with a polyester backbone and possessing some amount of double bonds may be utilized to some extend and is therefore included in the broad definition of an unsaturated polyester resin. These resins are employed in favor of reducing the price of the foam, to complete the mechanical properties of the foam and to add specific adhesion to the foam.

The unsaturated polyester resin must have good compatibility with UAO, lower viscosity and Tg similar to UAO.

A promising variant would be the result product of 1,2 Propylene Glycol with mixture of Phtalic and Maleic Anhydrides in ratio ≥ 2,5, diluted by efficient Acrylate or Methacrylate (mono or bi-functional).

1.3.4 Acrylic Type Foams

Generally, the feature to give foam on the expense of dissolved or suspended gas in its liquid state (monomer stage, melt or solution) is a common property of most of the known Polymers. There are several methods to perform it in order to respond to practical necessities and one of them is the Can Spray method. This method has found very successful application in the case of PU foams. Nevertheless there is one major disadvantage in this method – the final cure of those types of foams is provided by excess of free isocyanate, which is highly toxic. The acrylic type foams (**AT Foams**) are employed in order to overcome this disadvantage at the maximum preserving the good features of PU foams. It’s well-known that the majority of the good properties of the PU foams are due to the ability of containing urethane groups to form specific physical structures, provoked by the urethane group affinity to form unique net of H-bonds.

Therefore, to transfer the good characteristics of PU Foams to AT Foams at first is necessary that the monomer composition of the Froth is so completed, that the elements of PU Foams physical structure are available in AT Foams. The simplest way to ensure this is to use at dominant scale Acrylic terminated Urethane Prepolymers. Normal practice in PU foams is to prepare isocyanate terminated Prepolymers, containing 15% and more excess of NCO groups, which corresponds to 20% and more free MDI, if the question goes about MDI type of PU foams. This free MDI has many favorable functions:

1. Act as curing agents;
2. Reduce viscosity of the Froth by being a good solvent for NCO-terminated Prepolymers of MDI with Polyols with propoxy (PPG) – structure;
3. Act as blowing agent;

4. Agent, increase the gas acceptance in the Froth.

Unfortunately, in the Acrylic terminated stage MDI looses most of these functions. That’s why in the case of acrylic foams they have to be ensured in particular way in any separate case.

There is still one serious difference between PU Foams and AT Foams – in the way of polymerization, providing cure. Polyurethanes are products of Poly-condensation, where the Polymer is obtained by connecting at the expense of active groups and all monomer chain between two active groups joins to main Polymer chain. At some moment of this type Polymerization in the reaction system could be found in every intermediate product of the Process. Whereas in radical (thermal) Polymerization, typical of acrylates, only the acrylic group takes part in the main chain of the obtained Polymer, while other chains of the monomer, even when very long, remains lateral. In contrast to the Poly-condensation, at every moment the reaction system of radical polymerization can contain only ready polymer and non-reacted monomer. It’s easy to understand that mono-functional acrylate is able to give linear chains (in PU – two functional monomers) and bi-functional acrylates can give gel. But it’s very important to note that cross-linking with really controllable density and features can be provided when Poly-functional Acrylates take part in the system.

Therefore the mono-, bi- and poly-functional acrylic terminated Urethane Prepolymers should have the dominate part of Acrylics for the Froth of the AT – Foams.

As a rule, acrylic terminated urethane prepolymers have considerable higher viscosity in comparison to the respective OCN-terminated prepolymers. Specially, these on the base of MDI gives very often crystalline structures like pastes, very hard to suspend (in favor of spray process) and have very poor gas acceptance. As a result they either cannot spray alone or gives foams with expressed separation.

Therefore, the choice of active diluents is very important. The active diluents are acrylic mono, bi-, or tri-functional monomers, able to produce with the acrylic terminated urethane prepolymer, a transparent liquid with proper viscosity for the spray process, good acceptance toward the gas, not causing shrinkage and with contribution to the foam properties.

1.3.5 Readily available Backbones on Oligomers’ base

The scope of this research works spreads on the next high performance Backbones development:

1.3.5.1 CN9278B80

Aliphatic trifunctional Urethane Acrylate with 1,6 Hexane diol Diacrylate (1,6 HDDA, 20% by weight) as active diluent, a readily available product of Sartomer. This Oligomer is created in favor of photo curing composition. It suggested, according to the producer’s specification, solvent resistance, very good adhesion, good reactivity and flexibility. However, it is not specially created for Acrylic foams Backbone. It was selected for giving very promising foams, with serious advantages, but because of this, as a possible Backbone it needs to be improved in many aspects. Therefore it has to pass additional development to become commercial Backbone base. An addition of 10 – 15% of Polypropylene Triol 1300 Trimethacrylate (PPT1300TMA), lowering the viscosity, gives remarkable contribution to the quality of the foams in its base, but at the moment PPT1300TMA is still not commercially available.

1.3.5.2 PRO20652

Aromatic trifunctional Urethane Acrylate in 1,6 Hexane diol Diacrylate (20% by weight) active diluent, readily available and produced by Sartomer, as a response to Altachem’s requirement for an aromatic analog of CN9278B80. The expectations were that this Oligomer to give similar CN9278B80 results, to be less expensive and able to be improved by active diluents, different to the non-commercial PPT1300TMA. The first attempts with combination of SR423D and SR492 as active diluents gave promising results regarding to the final foam cell structure and toughness, but with many defects in the spray process. Indication is that a better selection of active diluents will make the backbone on this Oligomer base from High performance type, being less costly in comparison to CN9278B80 Backbone.

1.3.6 Synthesis of the newly created Backbone in Altachem

It is blend of acrylic terminated mono-, bi- and tri-functional MDI (p,p’ methylene di-phenyl di-isocyanate)

Mono-Functional Urethane Acrylate (**MFUA**) is composed by MDI molecules, in which the one of its NCO groups is transferred into consecution of Urethane and Acrylic group by 2-

Hydroxy Ethyl Acrylate (2-HEA) and the second NCO group is transferred into sole Urethane groups by mono-valent alcohol, such as 2-Ethyl Hexanol.

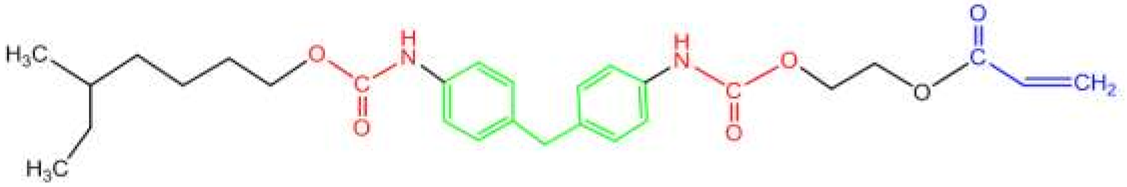


Figure 2 – Mono-Functional Urethane Acrylate

Bi-Functional Urethane Acrylate (**BFUA**) is composed by MDI molecules, in which either the both NCO groups are transferred into consecutions of Urethane and Acrylic groups by the use 2-HEA only or the same transfer ("harder" BFUA) is made, but the one of NSO is transferred by the use of 2-HEA and the second – by the use of Polypropylene Glycol 300 Mono-Methacrylate (PPG300MMA, SR604, PPM 5 LI, "softer" BFUA).

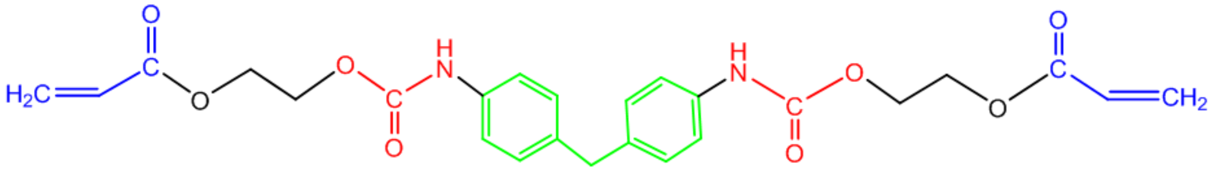


Figure 3 – Bi-functional Urethane Acrylate

Trifunctional Urethane Acrylate (**TFUA**) is Acrylic terminated (consecution Urethane, acrylic groups) Prepolymer of Glycerin with 3 moles MDI. The first of the terminations is made by use of SR604 (PPM 5 LI) and the next two are made by the use of HPMA. Thus the TFUA possesses 6 Urethane groups in its structure. The reason to use two different Hydroxy Acrylates for the termination is efficient to avoid brittleness in the foam. The reason to use HPMA instead of 2-HEA is to avoid preliminary formation of crystalline in the Froth, preventing proper spray process and Urethane – H bond NET formation during the cure.

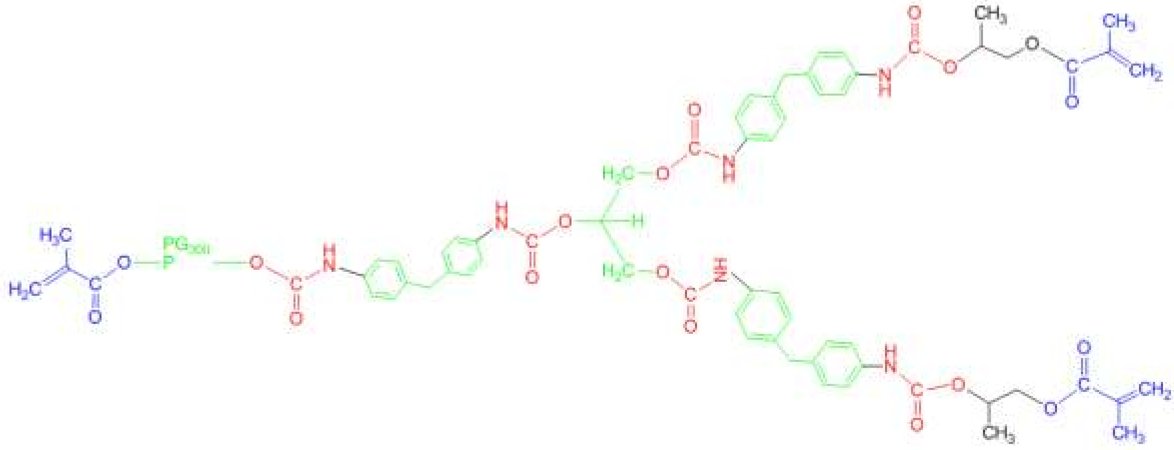


Figure 4 – Trifunctional Urethane Acrylate

The synthetic plan includes the blend of MFUA/BFUA to be obtained in the reactor first and afterward it serves as medium (being with lower viscosity) for further obtaining of TFUA.

The first step in preparation of MFUA/BFUA includes transferring MDI into mono-functional Isocyanate (see the picture below), adding to the load amount of crude MDI the calculated amount of 2-HEA (together with the necessary amount of active diluents) and mixing.

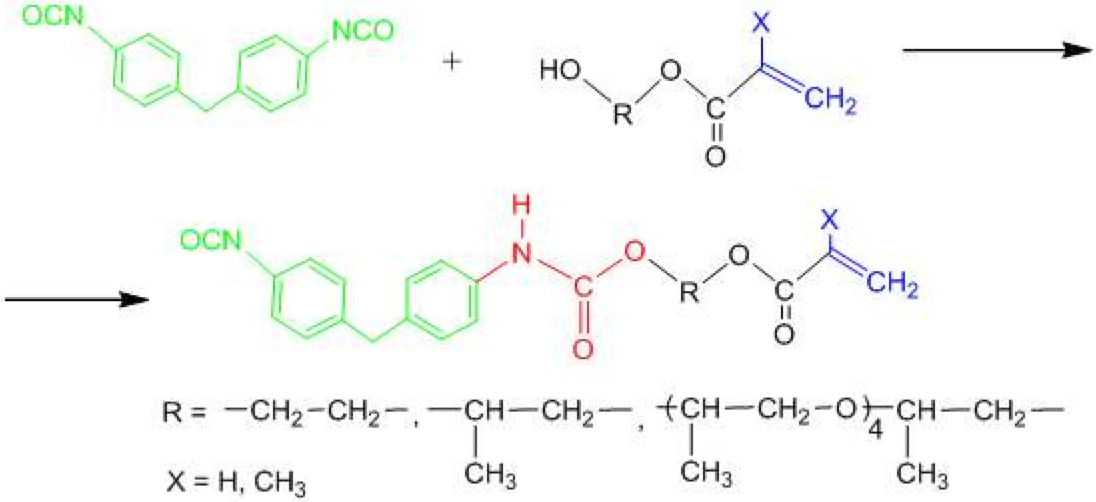


Figure 5 – Transferring MDI into Monofunctional Isocyanate

The reaction continues until the thermal liberation is sensitive (until the temperature of the cooling water at the way out of the reactor is still decreasing). In the second step, mixture of the calculated amounts of SR604 (PPM 5 LI) and 2-Ethyl Hexanol is added under mixing and the process continues until the thermal liberation is sensitive. At the end of MFUA/BFUA preparation, the content of free NCO groups in the medium must be lower than 0,1%.
Then, to the so prepared blend, the amount of crude MDI, calculated for TFUA, is loaded. At the first step for TFUA, the calculated amount of SR604 (PPM 5 LI) is added to it under mixing and the reaction continues until the thermal liberation is calming down. In the second step the calculated amount of HPMA is added, blended with the active diluents for TFUA, thus making the amount of MDI for TFUA mono-functional (see the picture above), regarding isocyanate activity. In the third step (after the thermal liberation stops) the calculated amount of Glycerin, mixed with the tri-functional active diluent (if this one is foreseen), is added under mixing and the reaction continues until the NCO content is still above 0,1% (some small additional amount of 2-HEA (HPMA) to adjust it bellow 0,1%, if necessary, is permissible).

Note: Generally, step 1 and 2 for TFUA could be combined, but then the indication about the end of the reactions, making MDI mono-functional Isocyanate, will be troubled (especially, with regards to full reaction of SR604).

All steps of the preparations are under mixing, propeller – turbine active element of the mixture is recommended because during the reactions the viscosity of the medium dramatically increases. Additional reason is that most of Hydroxy – reagents are hydrophilic, while MDI is hydrophobic, even Glycerin initially remains in heterogeneous phase.

All steps of the reaction are catalyzed by the use of Jeffcat T – 12 in concentration ~0,1%, which must be refreshed at every one of the additions respectively.
No heating system is necessary, the reactor must be equipped by water cooling jacked. If circulated cooling water is used, the thermal liberation warmth should be evacuated respectively on time so that the temperature of the cooling water could be the same at the way in of the reactor (to control the temperature at the way out in favor of finishing the steps). The temperature in the reactor shouldn’t reach more than 60°C. It’s not necessary to add the reagents to the reaction medium by strict portions, but the flow rate of loading must be considered with the permissible temperature.

The reactor may not need very strong defense against ambient moisture – reverse condenser, equipped with silica gel tube (or $CaCl_2$) may be enough.
After the Backbone is ready the access of ambient moisture is permissible, as no NCO groups are available. The ready Backbone should be stored in opaque, closed containers with non-metal internal surface, at temperatures between 4°C and - 10°C. Access of sun light is not permissible.

1.3.6.1 Main Prepolymer Synthesis

- Model CN927B80

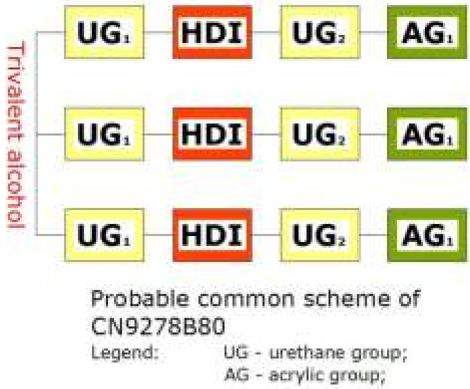


Figure 6 – CN927B80 Scheme

The common scheme of producing CN9278B80 most probable, includes:

Step1: Transferring the difunctional HDI into trifunctional, by the use of trivalent alcohol at the expense of the reaction with half of HDI NCO groups;

Step2: Transferring the so obtained Trifunctional isocyanate into acrylic terminated prepolymer by the use of monovalent alcohol, possessing the acrylic group, such as 2-Hydroxy Ethyl Acrylate or some similar, at the expense of the second half of HDI NCO groups;

The result, as it could be seen on the above presented scheme, is a trifunctional urethane acrylate. The presented 1,6 Hexane diol Diacrylate (SR238) is an active diluent with important function in the crosslinking polymerization.

- Model of MDI Prepolymer

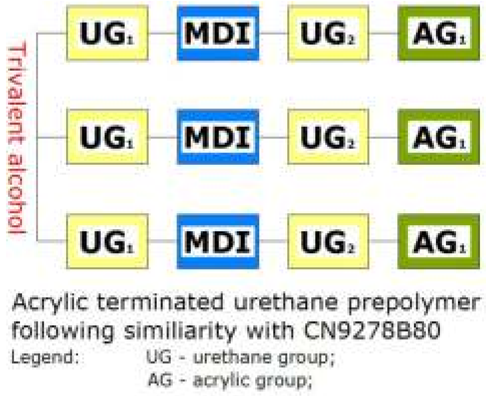
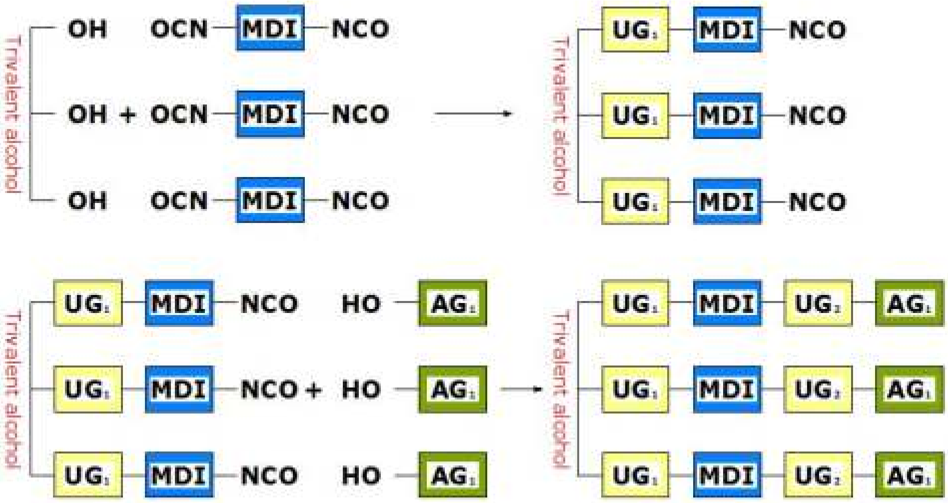


Figure 7 – MDI Prepolymer Scheme

The MDI prepolymer, so that to be similar to CN9278B80 template, must contain only the trifunctional urethane triacrylate and an active diluent with similar efficiency to the one that SR238 (1,6 Hexane diol Diacrylate) provides for CN9278B80. MDI model of CN9278B80 couldn’t be realized in any other distribution of NCO groups between the reagents except half (50%) of NCO for the trivalent alcohol and a second half for mono hydroxy acrylate. Otherwise, if the trivalent alcohol would react with more than half of NCO-groups, at first step (see above) the result will be gel. If the trivalent alcohol would react with less than half of NCO (presence of free MDI after the first step), at a second step the free MDI will give a third component – acrylic terminated MDI, which presence in the backbone is deviation from CN9278B80. Following the logic of the investigation, such deviation could be only accepted after the MDI recourses to give similar foam to that one of HDI (CN9278B80) are exhausted without acceptable result.

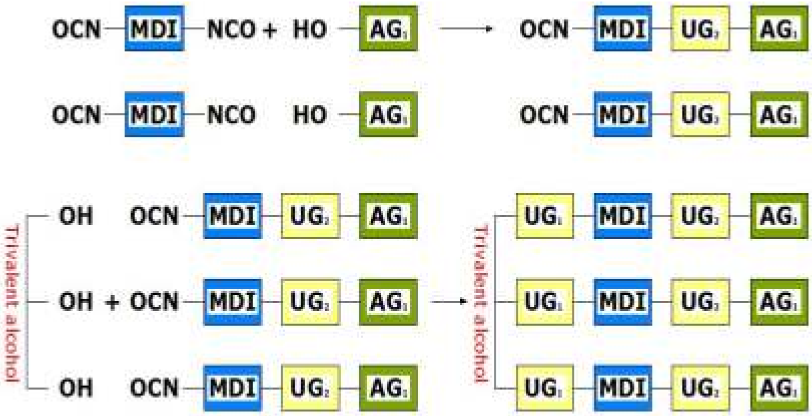
MDI gives prepolymers with high viscosity and in favor of the spray process active diluents are unavoidable necessary. Our attempts to use the active diluent, good working with CN9278B80, didn’t had satisfactory results. As a molecular content in the backbone system the MDI prepolymer as no more than 17%, although as weight is more than 70%. The rest molecular % up to 100% is for the active diluents. In fact, the MDI prepolymer is employed to give the skeleton of the foams with its high weight presence. But the active diluents can damage the foam properties due to their domination in the cure process, because of their high molar content (softness, shrinkage, post-expansion, etc.). Therefore, the main objects for investigation are, from the same priority, the components of the prepolymer (trivalent alcohol and hydroxy acrylate) and type and ratio of active diluents.



Reaction scheme 1: The trivalant alcohol reacts first with the MDI and the obtained trifunctional isocyanate reacts with acrylic group containing monovalen alcohol.
Investigated trivalant alcohols:
Rokopol G1000;
Rokopol G1500;
Glycerin.
Investigated acrylic group containing monovalent alcohols:
2-Hydroxy Ethyl acrylate;
Polypropylene Glycol (400) monomethacrylate, SR604.

Figure 8 – Reaction Scheme 1

At first sight above presented reaction scheme 1 is more logical than the reaction scheme 2. But without experimental determination of the really available NCO groups in MDI the calculated on the base of the given data amount of the trivalent alcohol surely will provide gelation. For this reason it’s also not possible to run the steps 1 and 2 together. During step 1, the viscosity grows very fast and the reaction goes into the diffusion area – as if it has finished, but in fact the viscosity slowly continues to grow.



Reaction scheme 2: The monovalant alcohol, containing acrylic groups, reacts first with MDI and the obtained monofunctional isocyanate reacts with the trivalant alcohol.
Investigated trivalant alcohols:
Rokopol G1000;
Rokopol G1500;
Glycerin.
Investigated acrylic group containing monovalent alcohols:
2-Hydroxy Ethyl acrylate;
Polypropylene Glycol (400) monomethacrylate, SR604.

Figure 9 – Reaction Scheme 2

The main problem in the reaction scheme 2 is the thermodynamic control onto the first step – MDI + Hydroxy Acrylate. Without urethane catalyst the reaction is very slow, but only with one drop Jeffcat T-12 it becomes very fast and if the liberated heat is not taken away in time, the result is gelation or huge viscosity. Without catalyst the reaction goes slow and ambient moisture takes considerable part in it, which will also result in high viscosity. Additionally, it is not possible to determine when the step 1 has finished without catalyst.

Nevertheless which of both reaction schemes would be chosen, more or less the synthesis is from molecular engineering type. Therefore some principles must be realized:

1. Every intermediate reaction surely to go to the end, i.e. to full exhaustion of one of the reagents
2. The product of every intermediate reaction to be determined qualitatively, as well as the possible lateral product, and the results to be estimated in view of giving the correct possibility for the next reaction in the scheme.

Therefore, some reactions, such as $-NCO + HO^-$, giving urethane group and leading to fast increase of the viscosity in the reaction medium, that on first sight are easy because of the high activity of the reagents, are in fact very difficult from the above presented principles point of view. In fact, the final result is, as if expected, but so deformed that the product is not able to execute the function for which it is employed and behaves in some rather unpredictable way.

1.4 Requirements for a Foam

A flexible foam, ready to be used in the do-it-yourself market, needs to comply some different aspects. Above all, the thermo mechanical behavior of the foam is important. These foams need therefore to pass several procedures, concerning the tensile strength, compression strength, shear strength, penetration of water, isolating capacity, etc. In the IFT-Rosenheim guideline (Institute for windows and doors), e.g., several European test norms are mentioned for the isolation of external windows and doors (34): the isolation needs to withstand weather conditions, opening and closing of windows, penetration of water, water vapor and air, fire. Isolative capacities, dimensional stability, etc. also need to be tested. On the other hand, since these foams are directly sold in

both the professional as the DIY market, user friendliness, cost and even appearance are important factors.
Since in a normal development phase one cannot hold all these different parameters into account at the same time, for OCF PUR foams, benchmarking tests were developed, holding several different parameters into account, shown in Table 4. These parameters, called response variables, include the analysis of sprayed material on paper and in a 2cm gap at two temperatures (e.g. 5 and 23 °C). These parameters consist in visual considerations of both the outside and inside of the foam, together with some applicability parameters. Shaking of the can indicates the mixing of the material in the can, forth shrinkage indicates the shrinking of the material when sprayed, froth outflow indicates the dimensional stability before curing (liquid stability), crumbling indicates vitrification during and/or after curing and glass bubbles is an indication of the surface structure (smooth or with glassy bubbles on the outside). "Side base holes" is an effect occurring in the 2 cm gap sprayed foam: blowing gas penetrates into the porous substrate (paper, wood or brick for real applications) and returns as a gas into the curing foam. This results in the appearance of holes at the side in the foam, reducing foam quality. Internal response variables include cell structure (fine-mazed or larger cell sizes), voids (the occurrence of larger voids in the foam), base holes (identical to side base holes, but occurring at the bottom of the foam), cell collapse (the coagulation of voids resulting in large, irregular shaped voids) and curing streaks (badly foamed cured pieces inside the foam result in hard segments).

Generally, it can be stated that the quality of a foam, and as a result physical characteristics, is improved if the cell size and structure are as small as possible, with the lowest amount of voids, base holes, cell collapse and no curing streaks (scoring all 5 out of 5). During this benchmarking test, the output out of the can is measured at the lower temperature. The output test is an applicability test where the amount of liquid (foam and readily evaporating blowing gas) and foam per second as well as gas loss at dispensing is measured. For the user, the output may either not be too low or too high, in order to fill gaps in the easiest way possible. It can be generally accepted that an output between 5 and 15 g/s is advisable.

Also, the foam density is measured of foam sprayed in the gap at the higher temperature. This density should be between 20 and 25 gram/liter, depending on the type of dispensing (gun or adapter). This density is also a cost factor. Suppose that in a 1000 ml can, filled with the obligated 750 ml product and a prepolymer density of 1g/l, the professional sprays his 750 g product with a foam density of 20 g/l, and another foam with a foam density of 30 g/l. The total yield in volume foam is then 750/20 g/(g/l) or, in the second case, 750/30 g/(g/l) or 37.5 l versus 25 l (33 % loss in total yield). So, for the user, it is advisable to lower the density, without causing a reduction in mechanical characteristics.

Parameter	***paper***		***2 cm gap***	
	Low temp	***High temp***	***Low temp***	***High temp***
External parameters				
Shaking can	3	3	3	3
Froth shrinkage	3	3		
Froth outflow	2.5	2.5		
Crumbling	5	3.5		
Glass bubbles	3	2.5	3	2.5
Side base holes			3.5	3.5
Internal parameters				
Cell structure	3	2.5	3	2.5
Voids and pin holes	2.5	2.5	2.5	2.5
Base holes	2.5	2.5	2.5	2.5
Cell collapse	4	3	4	3
Curing streaks	2.5	2.5	2.5	2.5

Table 4 - The different response variables used for the optimization of PUR foams sprayed on paper and in a gap at two different temperatures.

The development of a foam is performed using optimization software packages like Multisimplex® from Grabitech Solutions AB, which optimizes a foam with a given set of control variables (the chemical composition of the foam) and response variables (foam characteristics). Once for all different response variables threshold values or higher are obtained, thermomechanical tests are performed. Three basic physical tests are shown in Table 5. They include a compression test, a tensile strength test (or pull of test) and a shear strength test. In the pull of test: both adhesion of the foam and wooden substrate as tensile strength are tested: if the adhesion strength is lower than the tensile strength of the block, a breaking surface between the wood and foam will be observed. If the adhesion strength is higher than the tensile strength of the foam, tensile modulus of the foam is measured. In the point of view for the adhesion strength, it is evident the latter possibility is preferred if the required 80 kPa at the maximum strain is observed for the foam.

If a foam fails in one of these tests, new formulations need to be prepared. Of course, during the benchmarking test procedures, a clear direction in mechanical behavior can be readily investigated in a visual way.

Test	Description	Value
Compression test	Blocks with known dimensions are compressed at 5 mm/minute. At 10 % compression, the strain (kPa) is calculated.	30
Pull of test	the blocks are torn with a speed of 3 mm/min. The tensile strength at the maximum is calculated (kPa)	80
Shear strength test	The elongation at this maximum is calculated (%)	20
	Foam blocks are tested tangentially, the maximum shear strength is calculated (kPa)	25

Table 5 – Tests performed on PUR foams, together with some characteristic values (values are obtained as the average of at least 5 repeats).

Together with the physical testing, dimensional stability and accelerated aging tests are performed. In the dimensional stability test, the deformation of sprayed blocks is monitored as a function of time in different storage conditions: room temperature, -20 °C, 45 °C and 45 °C combined with a humidity of 90%. Only dimensional changes up to 4 % may be observed after a period of 5 weeks. In the accelerated aging tests, filled cans are stored at 45°C. Foam quality and output may not vary in a period of 6 weeks.

In the project, we want to create a foamed material with identical characteristics. We need therefore to achieve for both the visual response variables as well as all different mechanical, ageing and dimensional stability tests, identical or nearly identical results. Off course, in a first stage some of the parameters like cell structure will be most important to achieve first, other parameters can be considered to be less important. When the choice in backbone is made, all parameters need however to be fulfilled prior to a release on the market.

1.5 Ecofast Packaging Systems

1.5.1 Ecofast Packaging Systems for DIY

Figure 10 – Packaging Systems DIY for 1:10 and 1:1 mixing ratio

In the system formulated to 1:10 ratio the main disadvantage is the need to emptied all the aerosol can at once (Pot Life = +/- 15min).

1.5.2 Ecofast Packaging Systems for Professionals

Figure 11 – Packaging Systems for Professionals (2K Aerosol Can and Pressure Vessels)

1.6 Applications

- **Window Door Frames**

Quicker, stronger, cheaper and by 60% than mechanical fixing. No damage to the frame and no preparation or priming is required. It seals and insulates.

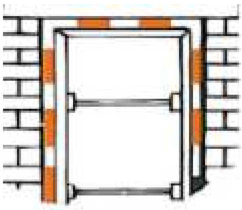


Figure 12 – Window Door Frames

- **Threshold and Sills**

An absolute weather proof seal can be produced which will not shrink or crack and is permanent.

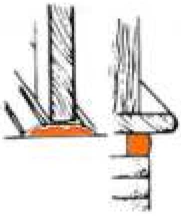


Figure 13 – Threshold and Sills

Duct Filling and Sealing

Where services enter a building it is possible for gases to enter causing serious hazards. A seal of foam in the duct will prevent this. A foam seal has been passed by the electricity council for this purpose.

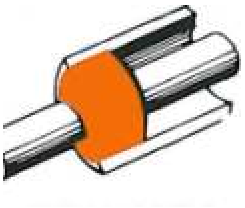


Figure 14 – Duct Filling and Sealing

Repairs

All types of buildings have holes and gaps which can be quickly and effectively filed with Alta foam.

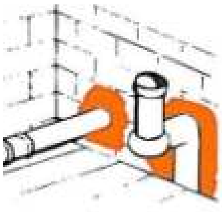


Figure 15 - Repairs

Roof Structure

Alta foam seals and prevents leakage. A common problem in many types of roof situations.

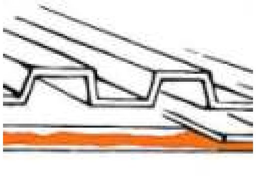


Figure 16 – Roof Structure

Floor and Panel Fixing

Floor boards can be sealed with Alta foam, preventing squeaks, pipes through joists set in foam will no hammer or creak. A few blobs of Alta foam will effectively and easily fix wall panels and skirtings.

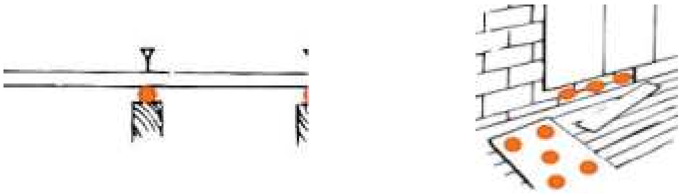


Figure 17 - Floor and Panel Fixing

Air Conditioning

A complete seal can be formed which reduces vibration and sound, as well as being insulating.

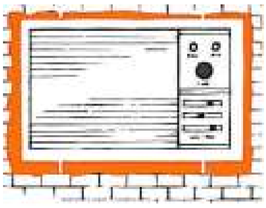


Figure 18 – Air Conditioning

2 Ecofast Foam Project

The development of new kinds of ecologically safe fast curing products is the main purpose of the Ecofast project. The target of the project is to develop an isocyanate monomer free formulation, giving similar properties to 1K PU foam.

It was chosen the model of radical polymerization in confrontation to the ionic polymerization due to the too long curing reaction of both cationic and anionic polymerizations.

Based on previously studies it was discovered that others oligomeric routes like resins based on polyester resins and on organic-acrylate resins gave bad results.

Meanwhile the radical polymerization of urethane acrylate oligomers seemed to be promising, especially the backbone based on the resin CN9278B80. The main disadvantage of this resin is the high price, due to its aliphatic isocyanate nature.

2.1 Experimental work

In order to achieve the objectives of this project, this work was divided in two routes, the first is dedicated to the study and optimization of the backbones based on the resin CN9278B80 and the resin PRO2005 (Route 1), the second is the synthesize of our own backbone based on aromatic urethane acrylates (Route 2), in order to overcome the disadvantage of the high price of the resins based on aliphatic isocyanate nature.

Route 1:

- Determination and adjustment of the reaction profile;
- Initiators and Accelerators Comparison;
- Study the influence of TCPP;
- Addition of some unsaturated esters and aromatic urethane acrylates in the formulation in order to make it cheaper;
- Optimization of formula with Multisimplex®;

Route2:

- Optimizing viscosity for spraying;
- Study of some variants with low viscosity to be used for active diluents;
- Optimizing composition to give appropriate foam (balancing mono- and bi-functional acrylics content);
- Optimization of the formula with the best results achieved;

The practical work includes the formulations made, all the analysis of the foams, either visual analysis or foams physical testing, density, and all the optimizations done or by comparison basis or by analyzing the results of all the tests performed.

The process of foaming of the froths on the newly created backbone is evaluated by measuring or evaluating the following parameters:

- ✓ Optimal content and amount of the used gas;
- ✓ Gas acceptance;
- ✓ Smoothness of the Spraying;
- ✓ Maximum level of emptying the Can;
- ✓ Fixture time of the foamed Froth;
- ✓ Maximum temperature of the cure process (for 10:1 version);
- ✓ Degree of homogeneity after the static mixer (for 1:1 versions);
- ✓ Spraying post-effects – stability of the foam before curing;
- ✓ Froth out flowing;
- ✓ Froth shrinkage (expansion) before starting the cure;
- ✓ Appearance of holes on the Froth surface before starting the cure;
- ✓ Side base holes.

The following characteristics of the obtained foam, are basic for its evaluation:

- ✓ Cell structure;
- ✓ Voids and pin holes;
- ✓ Crumbling;
- ✓ Cell collapse;
- ✓ Curing streaks;
- ✓ Sticky surface;
- ✓ Comparative Adhesion;

2.1.1 Execution risks

Crude MDI is not responding to the specification of the producer as regards to "Content of NCO equivalents" (% or eq. NCO/mol) because of moisture access or some other similar reason (i.e. passed shelf life, given by the producer) – all calculations, connected with the Backbone molecular design, are based on the credibility of this characteristics:

1. Hydroxy Acrylates to have passed some partial polymerization under storage staying or because of some other reason – Being mono-functional Acrylates, the partial Polymerization will slightly increase the viscosity only, but then this part of the product is not mono-functional yet (as regards to OH-activity) and becomes source of undesirable cure during the synthesis;

2. Storage stability of the Backbone itself – The synthesis includes reaction of NCO groups with OH-groups under the effect of catalyst and therefore both the thermal liberation and its intensity determine elevating temperatures in the reaction medium. In this way the used active Acrylates have to stay relatively long time under temperatures, unfavorable for their stability against undesirable Polymerization at storage staying before filling in cans or vessels;

3. Lateral reactions of MDI – Reactions of MDI with moisture or allophone reactions may occur under elevated temperatures that may be reached due to the NCO + OH catalyzed reaction's thermal liberation in the reaction medium. The effect on the Backbone will be undesirable jump in the viscosity and ratio MFUA/BFUA/TFUA not corresponding to the assigned. The used crude MDI – Suprasec 2004, is low reactive, but the addition of catalyst, as well the partial transfer of NCO groups, make it more active;

4. Stability in the Cans or Vessels under storage

   This kind of risk has two aspects:

   - Acrylic Backbone itself is able to perform partial polymerization in the Can under storage, which will provoke irreversible separation into pieces that are able to obstruct the nozzle during spraying and to stop it still at the beginning.

   - In the version 1:1 the Can B must contain the initiator, which is some peroxide. In this version it has to stay together with acrylics or some other liquid. Even active under elevated temperatures (120°C and higher) peroxides has restricted shelf life because of releasing (faster or slower) active radicals. If the Froth in Can B is not credibly inhibited (the speed of the radical neutralization is higher than the speed of their releasing), it either will cure or at least will provoke separation of the Froth, presented in the previous paragraph; However, too high concentrations of inhibitor in the Can B will exhaust the power of the initiator and after some period the cure of the sprayed foam will be either too slow or will be missing. Similar situation will appear if the peroxide is staying in the medium with relatively higher kinetic coefficient of the chain transfer, even at absence of double bonds.

5. Overheating at the activation the spray process – Production of high quality foams insists to use in the backbone Acrylates with higher functionality, combined with relatively long chains between the acrylic groups. This type polymerizing systems sometimes perform some difficulties with initiation, combined with following very sharp increase of the thermal liberation intensity. In these cases overheating the Froth is performed, which is strongly undesirable in version (10:1). The constructions of the cans, as well their endurance toward the pressure, allow max temperature in the can 60°C.

2.1.2 Blowing Agents

All the trials made have used a gas mixture of LPG (Liquid Petroleum Gases) – 30/0/70 (P/B/IB) and DME (30% of LPG) in 50% grams by volume of blend. The blowing agents give a cured foam with a certain density, has an influence on the dimensional stability of the cured foams and increases the shelf life of the product.

2.1.3 Specification's Products and Suppliers

The next tables present all the products that were used in the formulations, as well as some of its specifications.

Product	Details	MW (g/mol)	Density (g/cm^3)	Funct.	Supplier
CN 9278 B80	Aliphatic Urethane Acrylate	-	-	2	Sartomer
PRO2005	Aromatic Urethane Acrylate				Sartomer
PPT(1000)TMA	Polypropylenetriol Trimethacrylate	1000	1	3	IST
SR 238B	1.6 Hexanediol Diacrylate	226	1.02	2	Sartomer
SR 252	Polyethylene Glycol Dimethacrylate	770	1.101	2	Sartomer
SR 423D	Isobornyl Methacrylate	222	0.979	-	Sartomer
SR 454	Ethoxylated Trimethylolpropane Triacrylate	428	1.103		Sartomer

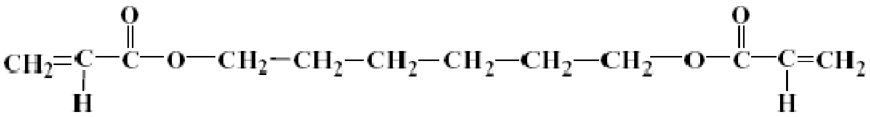
SR 494	Ethoxylated Pentaerythritol Tetraacrylate	528	1.128	4	Sartomer
SR 495B	Caprolactone Acrylate	344	1.1	1	Sartomer
SR 540	Ethoxylated Bisphenol Dimethacrylate	572	1.116	2	Sartomer
SR 604	Polypropylene Glycol Monomethacrylate	376	1.01	1	Sartomer
SR 610	Polyethylene Glycol Diacrylate	742	1.117	2	Sartomer
SR 9020	Propoxylated Glyceryl Triacrylate	428	1.089	3	Sartomer
Synocure 505	Unsaturated polyester*	-	-	-	Cray Valley
2-EH	2-Ethylhexanol	130.23	0.833	1	Aldrich
2-HEA	2-Hydroxy Ethyl Acrylate	116	1.01	1	Rohm&Haas

Table 6 – Resins and Crosslinkers

CN9278B80 is a ***trifunctional aliphatic urethane acrylate, diluted in HDDA (SR238),*** for use in ultra violet and electron beam curing compositions. It offers the following key properties to your formulations, excellent solvent resistance, very good adhesion, good reactivity and flexibility

PPT(1000)TMA and the information on the table is the information available.

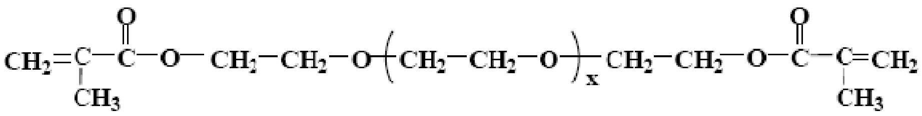
SR238B, 1,6-hexanediol diacrylate, is a low viscosity, fast curing monomer with low volatility, a hydrophobic backbone, and good solvency for use in free radical polymerization.



$$CH_2=\underset{H}{C}-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-\underset{H}{C}=CH_2$$

Figure 19 – 1,6-Hexanediol Diacrylate

SR252, polyethylene glycol (600) dimethacrylate, is a water soluble difunctional monomer that produces soft, flexible films.



$$CH_2=\underset{CH_3}{C}-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O\left(CH_2-CH_2-O\right)_x CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{C}=CH_2$$

Figure 20 – Polyethylene Glycol (600) Dimethacrylate

SR423D, Isobornyl Methacrylate, is a monofunctional monomer with a cyclic group which offers a high glass transition temperature. It has a refractive index of 1.4738. SR423D is recommended for use in metal coatings, structural adhesives, and as a chemical intermediate.

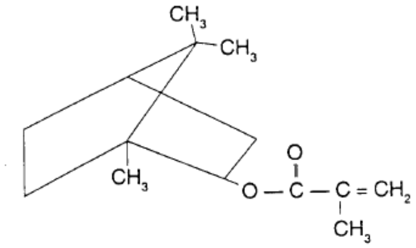


Figure 21 – Isobornyl Methacrylate

SR-454, 3 mole ethoxylated trimethylolpropane triacrylate, is a low skin irritation, fast curing monomer for use in free radical polymerization.

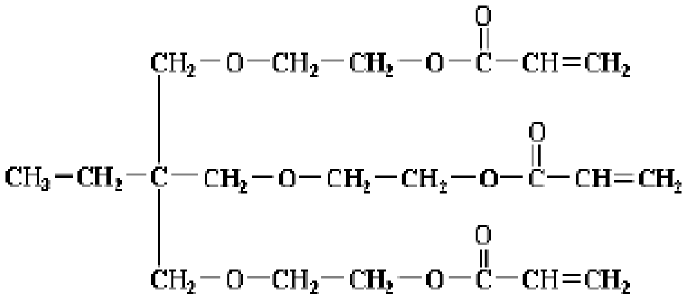


Figure 22 – 3-mole Ethoxylated Trimethylolpropane Triacrylate

SR-494, ethoxylated pentaerythritol tetraacrylate, is a heat resistant, fast curing tetrafunctional monomer for use in UV/EB polymerization. It is a low skin irritation monomer.

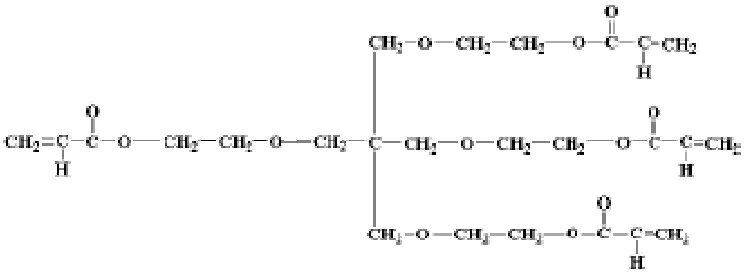
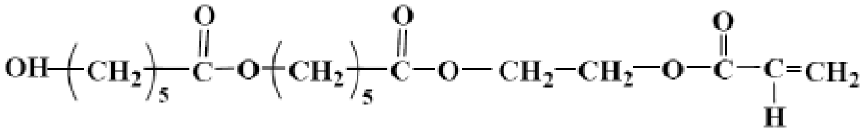


Figure 23 – Ethoxylated Pentaerythritol Tetraacrylate

SR495B, caprolactone acrylate, is a low skin irritation, low volatility, and low odor, monofunctional monomer for use in UV/EB or cationic curing.



$$\mathrm{OH}\left(\mathrm{CH_2}\right)_5\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}-\mathrm{O}\left(\mathrm{CH_2}\right)_5\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}-\mathrm{O}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{O}-\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}-\underset{\underset{\displaystyle H}{|}}{\mathrm{C}}=\mathrm{CH_2}$$

Figure 24 – Caprolactone Acrylate

SR540, ethoxylated (4) bisphenol A dimethacrylate is a low volatility monomer used in free radical polymerization. It provides a good hydrophobic and hydrophilic balance.

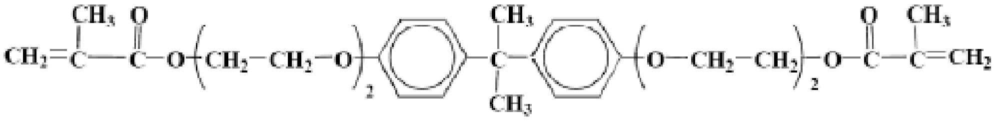
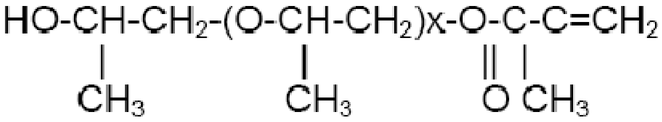


Figure 25 – Ethoxylated (4) Bisphenol A Dimethacrylate

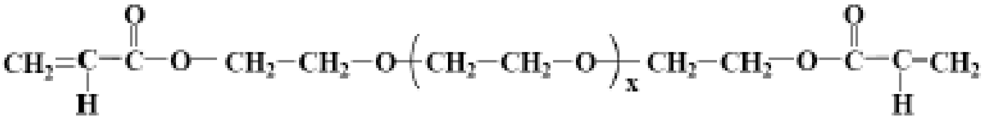
SR604, Polypropylene Glycol Monomethacrylate, is a monofunctional monomer, with flexibility and low shrinkage. It has a dual functionality and can be used in dual cured systems. SR604 is recommended for use in adhesives, cosmetics, electronics and photopolymers.



$$\mathrm{HO}-\underset{\underset{\displaystyle CH_3}{|}}{\mathrm{CH}}-\mathrm{CH_2}-(\mathrm{O}-\underset{\underset{\displaystyle CH_3}{|}}{\mathrm{CH}}-\mathrm{CH_2})\mathrm{x}-\mathrm{O}-\underset{\underset{\displaystyle O}{\|}}{\mathrm{C}}-\underset{\underset{\displaystyle CH_3}{|}}{\mathrm{C}}=\mathrm{CH_2}$$

Figure 26 – Polypropylene Glycol Monomethacrylate

SR610, polyethylene glycol (600) diacrylate, is a low skin irritation, water-soluble monomer that produces soft, flexible free-radically cured flexible films.



$$\mathrm{CH_2}=\underset{\underset{\displaystyle H}{|}}{\mathrm{C}}-\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}-\mathrm{O}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{O}\left(\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{O}\right)_x\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{O}-\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}-\underset{\underset{\displaystyle H}{|}}{\mathrm{C}}-\mathrm{CH_2}$$

Figure 27 – Polyethylene Glycol (600) Diacrylate

SR9020, 3-mole propoxylated glyceryl Triacrylate is a trifunctional monomer offering low viscosity, good flexibility, fast curing, and excellent hardness.

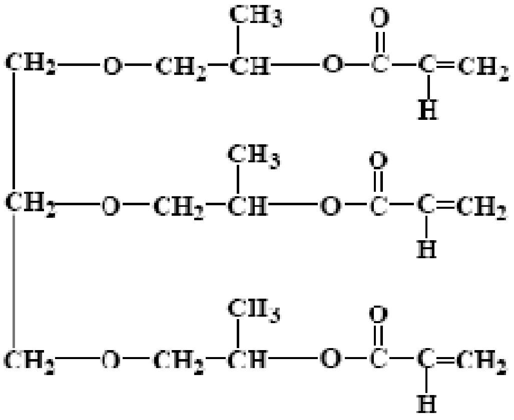


Figure 28 - 3-mole Propoxylated Glyceryl Triacrylate

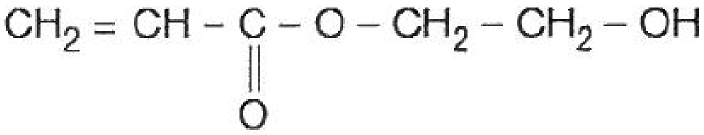
Synocure 505 the following table presents the components of the resin which were given by the supplier.

Composition Synocure 505	ppt	%
E 9015 UPR base	369	36,9
CN 104 epoxy acrylate	184	18,4
Triethylene glycol vinyl ether	332	33,2
Diethylene glycol vinyl ether	111	11,1
Bisomer PTE	4	0,4

Table 7 - Composition of the Synocure 505

2-EH, 2-Ethylhexanol is most commonly used in production of phthalates for rubber and plastic fabrication. It is a good paint solvent and an active component of textile finishing formulation, acrylate and additives for diesel fuel and lube oil.

2-HEA, 2-Hydroxyethyl Acrylate is an acrylic ester containing hydroxyl groups, for manufacturing polymers and for use as feedstock for synthesis.



$$CH_2 = CH - \underset{\underset{O}{\|}}{C} - O - CH_2 - CH_2 - OH$$

Figure 29 - 2-Hydroxyethyl Acrylate

Product	Details	MW (g/mol)	Density (g/cm^3)	Supplier
B 8870	-	1870	1	Degussa
Paraffin	General formula: C_nH_{2n+2}	-	0,93	Aldrich
FCA 400	Emulsifier Polyurethane Foam	-	1,12	BYK-Chemie
TCPP	Tris (Chloro-isoPropyl) Phospahate	327.57	1,29	EcoChem

Table 8 - Silicones, additives and flame retardants

B8870 is a silicone and his function is decrease the surface tension of the polymer mix. An optimum stability is obtained when the surface tension reaches the lowest value possible. Not adding B8870 causes froth collapse before the polymer reaches the curing time. The presence of silicone promotes good shape of the foam and a good cell structure, but an excess of silicone cause the surface of the foam to be stick.

Paraffin is used in order to confer more viscosity to the mixtures, which allow the foam to have a more flexible and resilient structure. So in this case we can consider paraffin as a thickening agent because increases viscosity without substantially modify other properties. The use of paraffin causes a hardening of the foam structure, increases adhesion, reduces the shrinkage and promotes the stiffness of the final product.

FCA 400 is an emulsifier and the function of this additive is to reduce the interfacial surface tension. To enhance a good mixing of the resin and blowing gas resulting in a blown up structure an emulsifying agent needs to be added. When using emulsifier large cell structure is obtained, more expansion is observed leading to a lower density and the foam surface is less brittle.

The **TCPP** is a flame retardant additive, besides the flame retardant function it is also used to soften the structure and improve adhesion. An excess of TCPP leads to a big outflow, shrinkage and some interior bubbles.

Product	Details	MW (g/mol)	Density (g/cm^3)	Supplier
Bisomer PTE	N,N-Bis-(2-hydroxyethyl)-para toluidine	217	1.11	Cognis
Accelerator VN-2	Vanadium monobutyl dihydrophosphite, 0.2% V		1.160	AkzoNobel
Accelerator NL-49P	Cobalt (II) 2-ethylhexanoate, 1% Co, in aliphatic ester		0.949	AkzoNobel
Perkadox L-W40	Dibenzoyl peroxide 40% suspension in water	242.2	1.10	AkzoNobel

Perkadox CH-50L	Dibenzoyl peroxide 50% with dicyclohexyl phtalate	242.2	-	AkzoNobel
Butanox LA	Methyl ethyl ketone peroxide, in phthalate mixture		1.085	AkzoNobel
Butanox M-50	Methyl ethyl ketone peroxide, in dimethyl phthalate		1.18	AkzoNobel

Table 9 – Activators and Initiators

Bisomer PTE is an aromatic tertiary amine used as an amine activator for organic peroxide initiation, ideal for use in formulations utilizing dibenzoyl peroxide. Bisomer PTE is extensively used in activating MMA based acrylic resins.

Accelerator VN-2 is a vanadium based accelerator for the cure of unsaturated polyesters resins, vinylesters resins and (meth) acrylic resins in combination with ketone peroxides and hydroperoxides. In combination with ketone or hydroperoxides short gel times and fast cure rates can be obtained.

Accelerator NL-49P is a cobalt based accelerator (1% cobalt in aliphatic ester) for the cure of unsaturated polyesters resins in combination with ketone peroxides, cyclohexanone peroxides and acetylacetone peroxides.

Perkadox L-W40 can be used as initiator for the solution copolymerization) of acrylates and methacrylates in the temperature range of 80-150ºC, amongst others for manufacture of coatings.

Perkadox CH-50L can be used for the polymerization of diethylene glycol diallylcarbonate) based optical monomers and is especially recommended for sunlenses.

Butanox LA is a methyl ethyl ketone (MEKP) for the curing of unsaturated polyester resins in the presence of a cobalt accelerator. Is particulary suitable for the curing of gelcoats resins, laminating resins and lacquers when a longer gel time is required.

Butanox M-50 is a general purpose MEKP for the curing of unsaturated polyester resins, laminating resins, lacquers and castings.

Product	Details	MW (g/mol)	Density (g/cm^3)	Funct.	Supplier
Castor Oil		932	0.956	3	Vandeputte
Rokopol D1002		1000	1.02	2	PCC Rokita
Rokopol G1000		1000	1.02	3	PCC Rokita
Rokopol TG500		500	1.05	3	PCC Rokita
Glycerin		93.09	1.261	3	Brenntag

Table 10 – Polyols

Castor Oil is a relatively inexpensive and renewable source of hydroxyl groups. This makes use of castor oil in polyols for polyurethane very attractive. We have prepared a simple castor oil based polyol for rigid polyurethane foam application. The polyol is a physical blend of castor oil and glycerol. Glycerol acts as a cross-linker which gives the foam sufficient rigidity and reduces shrinkage.

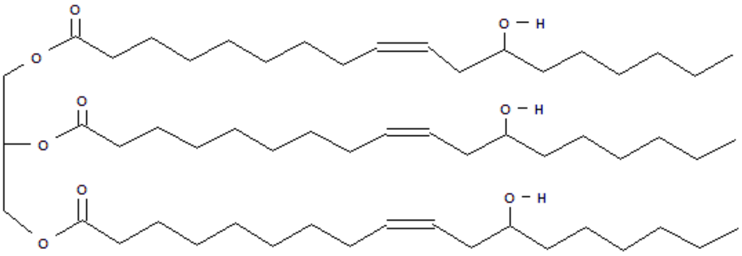


Figure 30 – Castor Oil

Rokopol D1002 is a high purity polyoxypropylene glycol of molecular weight 1000. It is designed as an intermediate for the production of polyurethane elastomers, coatings, adhesives, foams of special features and as one of the main raw materials for spray-on (mist) coating manufacture.

Rokopol G1000 is a high purity polyoxypropylene triol of molecular weight 1000. It is designed as an intermediate for the production of polyurethane elastomers, single spray foam, coatings, adhesives, impregnants and varnishes.

Rokopol TG500 is a high purity polyoxypropylene triol of molecular weight 500. It is designed as an intermediate for the production of polyurethane elastomers, coatings, adhesives, impregnates and varnishes. Rokopol TG500 is sometimes used as the major polyol in certain high density rigid moulding systems.

Product		Details	MW (g/mol)	Density (g/l)
DME (Dimethyl ether)		CH_3OCH_3	46,07	1,97
LPG	Propane	C_3H_8	44,096	1,83
	Isobutane	C_4H_{10}	58,12	2,51

Table 11 – Blowing Agents

DME or dimethyl ether is used as a propellant in aerosols. It is also a solvent, and a fuel used in welding. It also finds use as a refrigerant. It has an anesthetic effect in high concentrations.

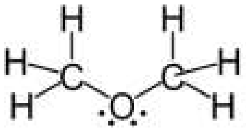


Figure 31 – DME

LPG or liquefied petroleum gas is a mixture of hydrocarbon gases used as a fuel in heating appliances and vehicles, and increasingly replacing chlorofluorocarbons as an aerosol propellant and a refrigerant to reduce damage to the ozone layer. Varieties of LPG bought and sold include mixes that are primarily propane or butane or even a mix of both. In this study, the LPG used was with a ratio of 30% Propane and 70% Isobutene.

2.1.4 Density Testing (35)

For PU foams, the overall density mould (ODM) was the method that was used for the measurement of density. This method is based on the Archimedes' Principle.

- Archimedes’ Principle

Archimedes' Principle says that the apparent weight of an object immersed in a liquid decreases by an amount equal to the weight of the volume of the liquid that it displaces. Since 1 ml of water has a mass almost exactly equal to 1g, if the object is immersed in water, the difference between the two masses (in grams) will equal (almost exactly) the volume (in ml) of the object weighed. Knowing the mass and the volume of an object allows us to calculate the density

Figure 32 – Archimedes' Principle

2.1.5 Physical testing's

It was performed different tests as compression, adhesion and shear strength using moulds as the ones represented below.

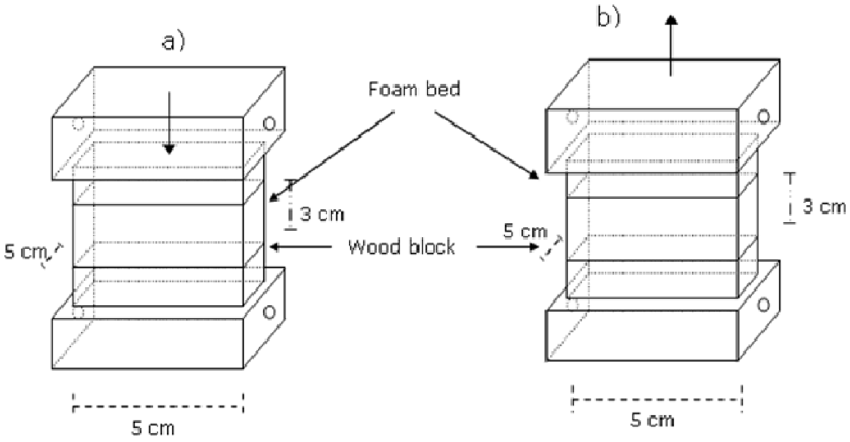


Figure 33 – Compression (a) and Adhesion (b) tests

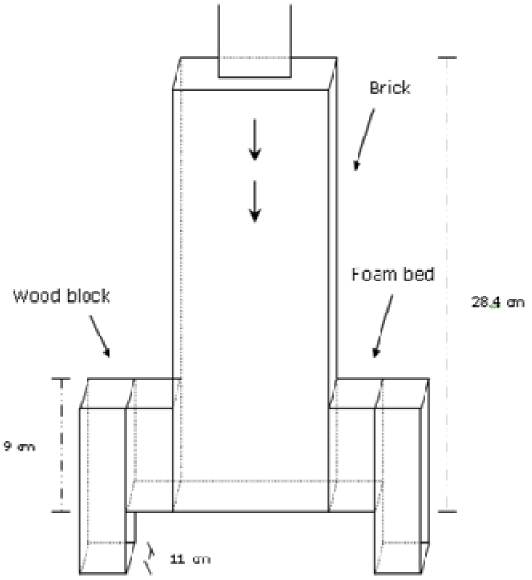


Figure 34 – Shear Strength Test

These tests were not performed for all foams obtained. However, they were useful to study the influence of the silicone as well as the paraffin, in the mechanical properties of the foams.

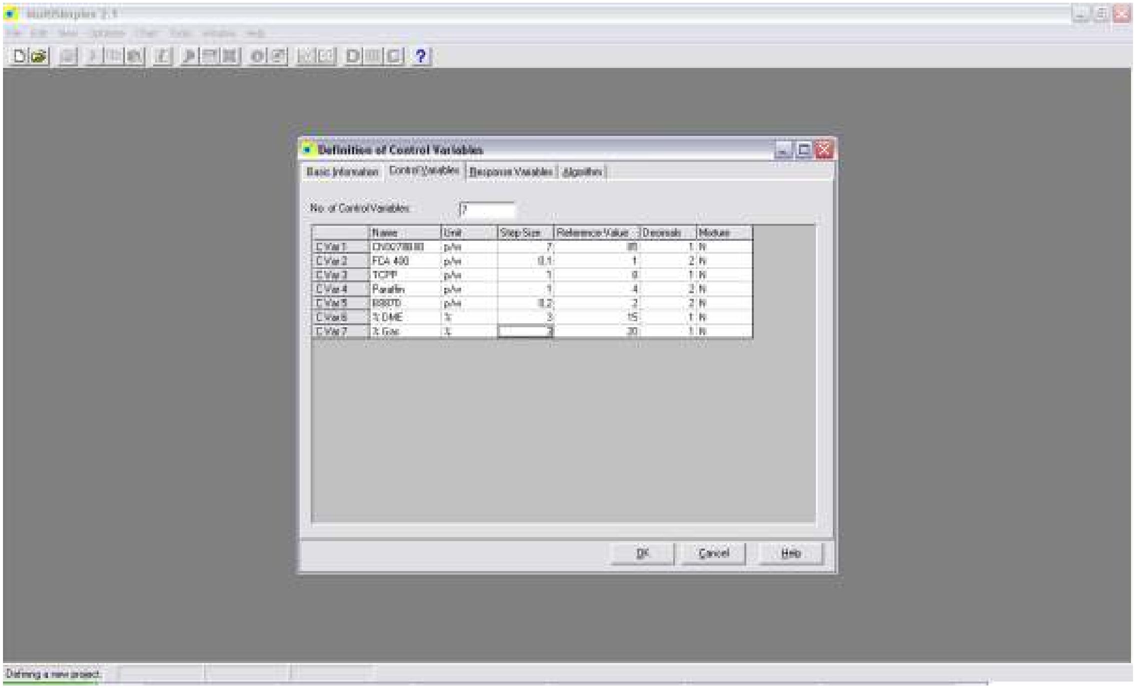
2.1.6 Influence of new additives on overall foam quality

To determine the influence of new additives on the overall foam quality a technical system, Multisimplex®, to optimize the foams quality is used. This system consists in systematical adjustment the control variables to the levels of achieving the best possible outcome (response). Usually, many conflicting responses must be optimized simultaneously. In lack of systematic approaches the optimization is done by "trial-and-error", or by changing one control variable at a time while holding the rest constant.
In the present project the following control variables are defined:

- ✓ the content by weight or by weight parts of **B8870**, the foam stabilizer before the cure;
- ✓ the content by weight or by weight parts of **FCA400**, dispersing agent;
- ✓ the content by weight or by weight parts of **solid paraffin**, having effect on the shrinkage level and the foam adhesion;
- ✓ the content by weight or by weight parts of **TCPP, flame retardant**, having effect as the foam plasticizer and regulator of the Froth viscosity;
- ✓ % **Gas** by volume, having effect on the foam density and shrinkage;

- ✓ % **DME** in the gas mixture, having effect on the .

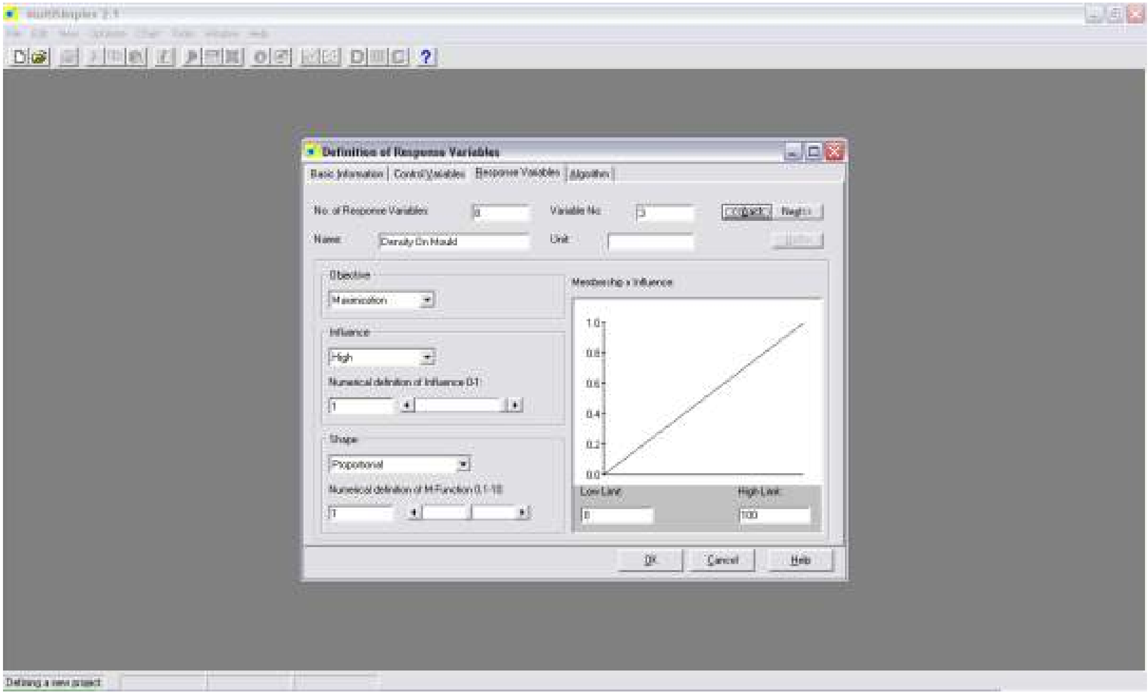
As response variables we have determine them to be shrinkage, ODM, brittleness, compression strength, adhesion strength and shear strength.



No. of Control Variables: 7

	Name	Unit	Step Size	Reference Value	Decimals	Medium
CVar 1	DV00780.00	p/w	7	80	1	N
CVar 2	FCA 400	p/w	0.1	1	2	N
CVar 3	TCPP	p/w	1	9	1	N
CVar 4	Paraffin	p/w	1	4	2	N
CVar 5	B8070	p/w	0.2	2	2	N
CVar 6	% DME	%	3	15	1	N
CVar 7	% Gas	%	3	20	1	N

Figure 35 – Definition of the Control Variables in the Multisimplex®



No. of Response Variables: 6

Variable No: 3

Name: Density On Mould

Unit:

Objective: Maximization

Influence: High

Numerical definition of Influence 0-1: 1

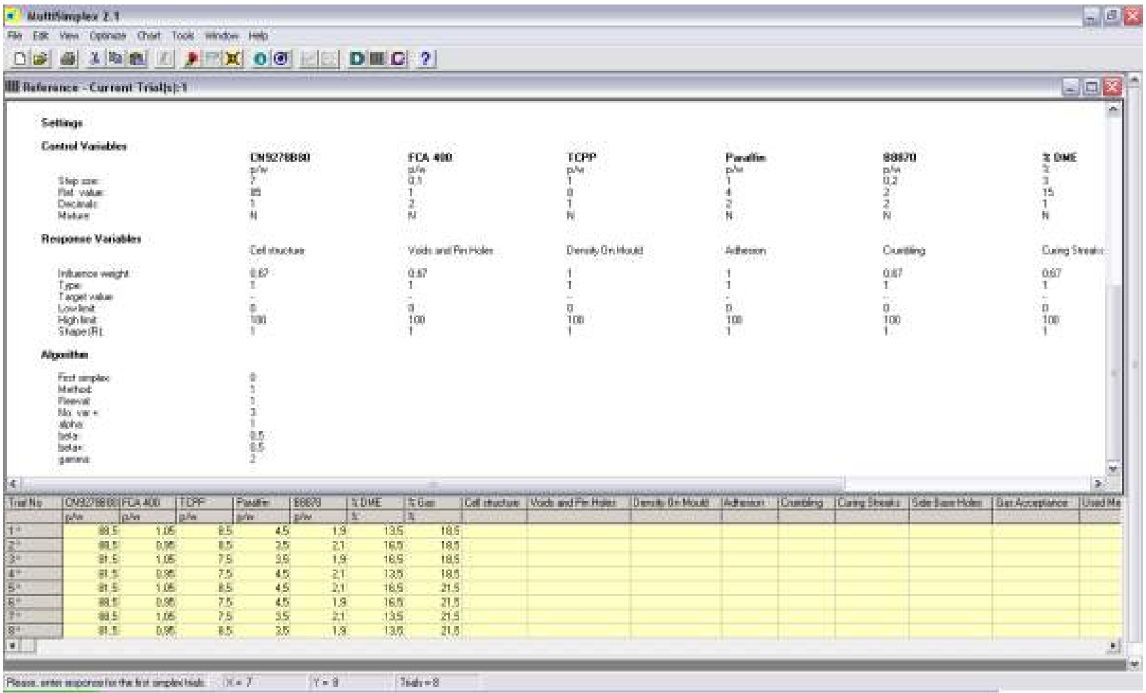
Shape: Proportional

Numerical definition of M-Function 0.1-10: 1

Low Limit: 0

High Limit: 100

Figure 36 – Definition of the Control Variables in the Multisimplex®



Settings

Control Variables

	CN9278B80	**FCA 400**	**TCPP**	**Paraffin**	**B8870**	**% DME**
	p/w	p/w	p/w	p/w	p/w	%
Step size:	7	0.1	1	1	0.2	3
Ref. value:	85	1	8	4	2	15
Decimals:	1	2	1	2	2	1
Mixture:	N	N	N	N	N	N

Response Variables

	Cell structure	Voids and Pin Holes	Density On Mould	Adhesion	Crumbling	Curing Streaks
Influence weight:	0.67	0.67	1	1	0.67	0.67
Type:	1	1	1	1	1	1
Target value:	-	-	-	-	-	-
Low limit:	0	0	0	0	0	0
High limit:	100	100	100	100	100	100
Shape (R):	1	1	1	1	1	1

Algorithm

First simplex:	0
Method:	1
Reeval:	1
No. var +:	3
alpha:	1
beta:	0.5
beta+:	0.5
gamma:	2

Trial No	CN9278B80	FCA 400	TCPP	Paraffin	B8870	% DME	% Gas	Cell structure	Voids and Pin Holes	Density On Mould	Adhesion	Crumbling	Curing Streaks	Side Base Holes	Gas Acceptance	Used Me
	p/w	p/w	p/w	p/w	p/w	%	%									
1*	88.5	1.05	8.5	4.5	1.9	13.5	18.5									
2*	88.5	0.95	8.5	3.5	2.1	16.5	18.5									
3*	81.5	1.05	7.5	3.5	1.9	16.5	18.5									
4*	81.5	0.95	7.5	4.5	2.1	13.5	18.5									
5*	81.5	1.05	8.5	4.5	2.1	16.5	21.5									
6*	88.5	0.95	7.5	4.5	1.9	16.5	21.5									
7*	88.5	1.05	7.5	3.5	2.1	13.5	21.5									
8*	81.5	0.95	8.5	3.5	1.9	13.5	21.5									

Please, enter responses for the first simplex trials | X = 7 | Y = 8 | Trials = 8

Figure 37 – Optimization of the formulations based on the reference

2.1.7 Alta Foam Monitor Reports

To understand the physic-chemical reactions and physical changes in a curing OCF froth several parameters can be studied. The most significant physical parameters of a foam are the curing speed and the expansion of the froth. Therefore the height and curing speed are measured.

A good adhesion of the foam to the substrate is another important parameter and can be linked with the pressure developed by the foam.

Since the chemical reactions that occur in the foam are exothermal, the initial expansion of the foam is exothermal and the initial expansion of the foam is based on the evaporation of liquid gas, the measurement of the temperature will also reveal important insights.

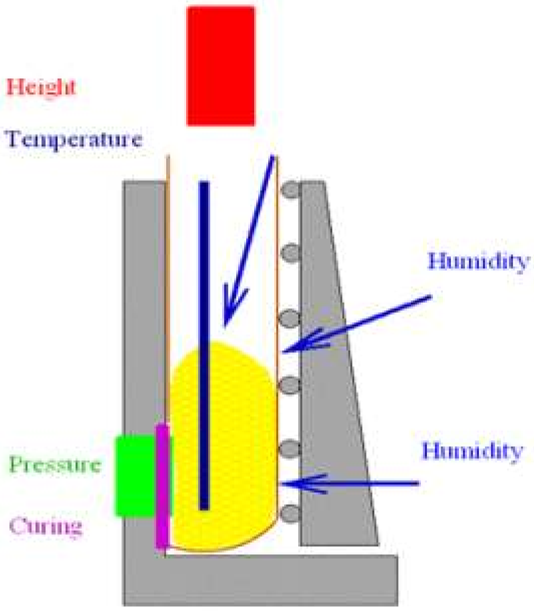


Figure 38 – Measured properties while the FROTH/FOAM is curing

Since the curing reaction is very sensitive to changes in temperature and humidity, all tests should be done under constant enviromental conditions.

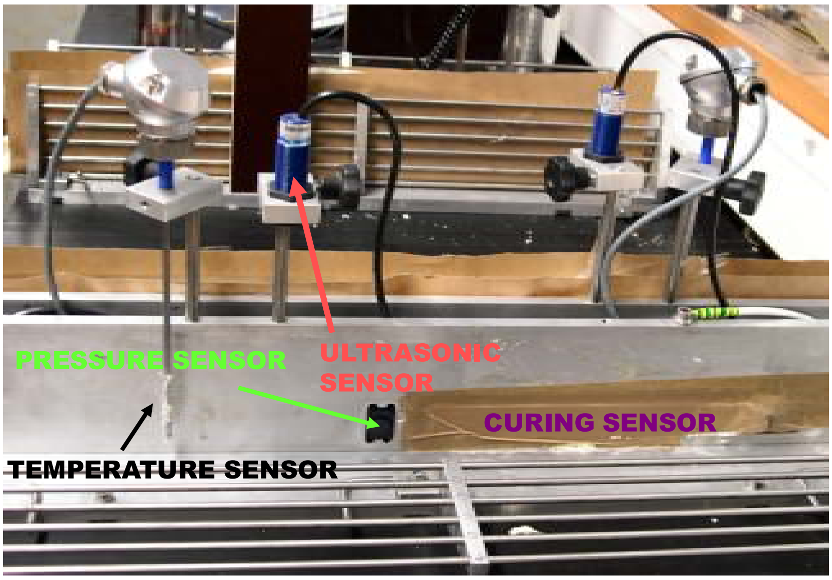


Figure 39 – Mold with used sensors

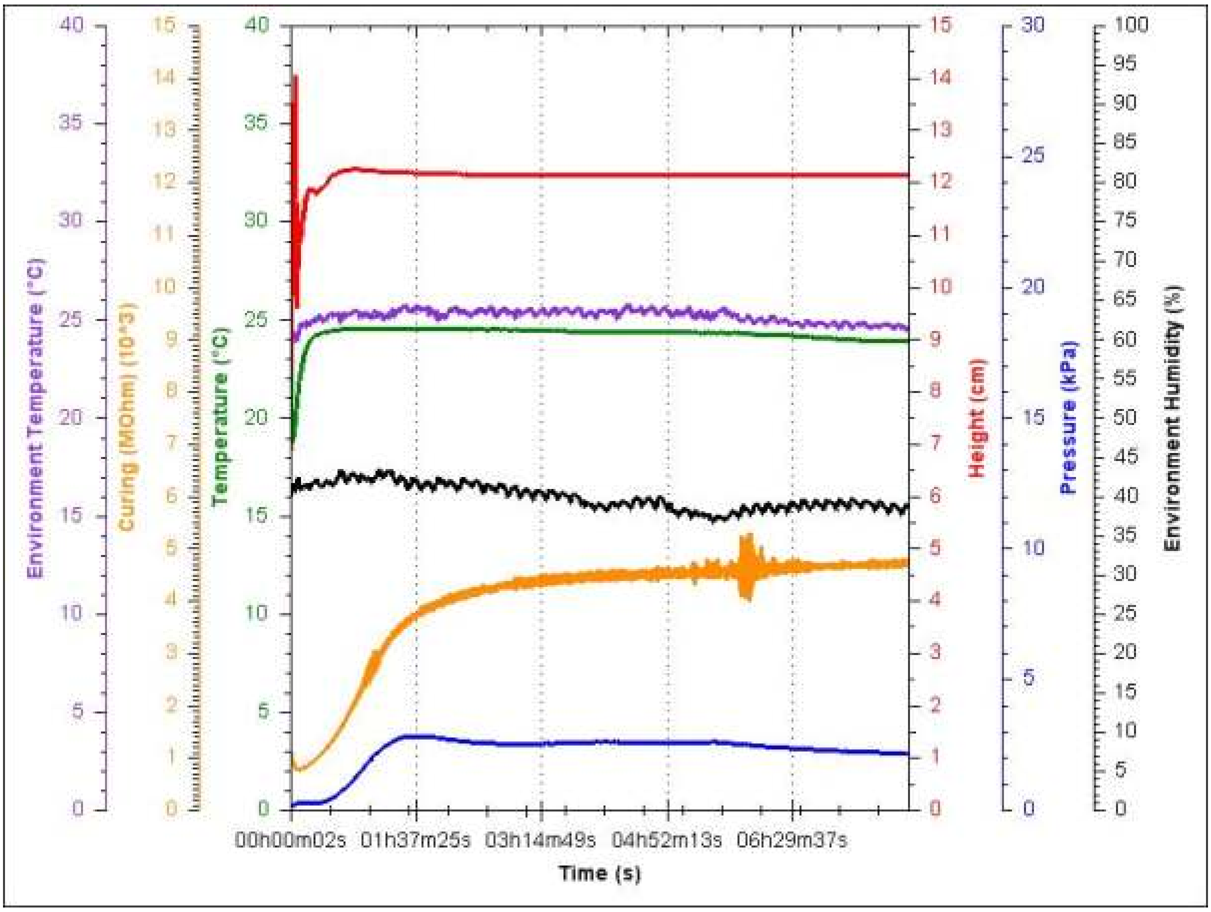


Figure 40 – Report Overview

The previous pages shows a general overview of the results during the first 24 hours of the test. The pages contain the report on the different aspects of the measurement: Temperature, Post Expansion, Pressure and Curing.

When a slow expanding foam is dispensed in the mould the temperature graph sometimes shows a slow slope downwards due to the slow rising foam that is surrounding the sensor.

2.2 Experimental Results

2.2.1 Route1

The possible future chemical backbone will consist in unsaturated oligomers system. Starting preferably with no smelling and no hazardous oligomers, initiators and accelerators will be added to promote the crosslink reaction. It is expected the need of rheology modifiers (to adjust froth stability), tackifiers, silicon surfactants and blowing agent to prepare a complete formulation.

Using this formulation as reference several cases were studied in order to obtain the best results possible according to the purpose of this study.

	Compounds	Parts / weight
Aliphatic Urethane Acrylate	CN 9278B80	90
Crosslinker	PPT1000TMA	10
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	Paraffin	4
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	2

Table 12 – Formulation A1

2.2.1.1 Determination and adjustment of the reaction profile

The main purpose of the reactivity tests is to control the gel point, as well as the peak temperature, since due to aforementioned reasons (and also safety ones) it shouldn't be higher than 60°C and less than 7min.

- **Perkadox CH-50L: Bisomer PTE** – (Initiator: Accelerator)

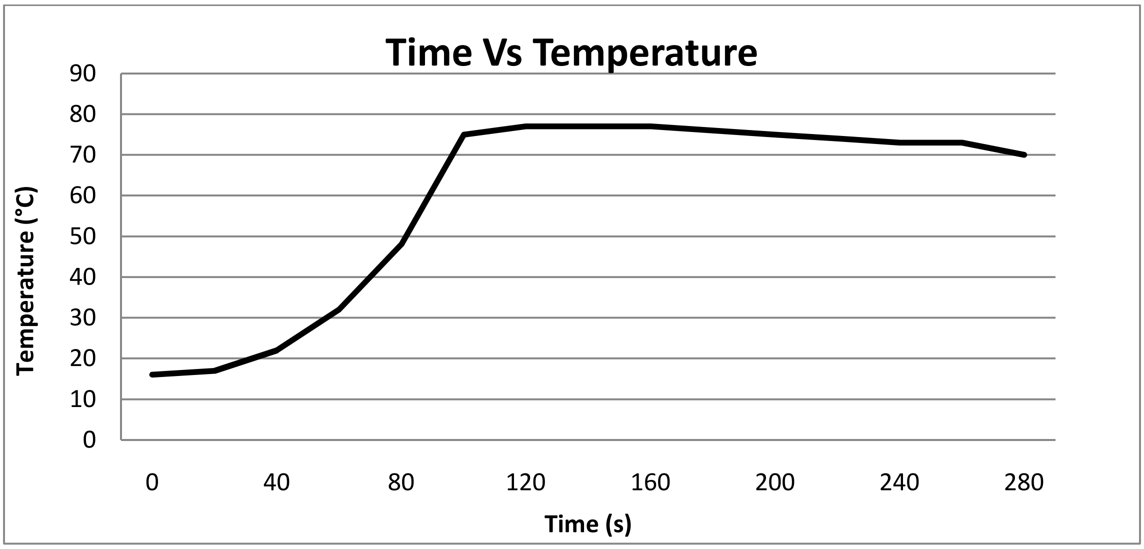


Figure 41 – Reaction Profile of the Pair 1 (4pbw: 2pbw) for the formulation A1

An adjustment in the quantity of the accelerator and initiator in a constant form is needed to adequate the speed reaction.

Sample	Initiator (pbw)	Accelerator (pbw)
S0001	1	1
S0002	2	1
S0003	3	1
S0004	4	1
S0005	1	2
S0006	2	2
S0007	3	2
S0008	4	2
S0009	1	3
S0010	2	3
S0011	3	3
S0012	4	3

Table 13 – First Taguchi Trial Setup for the Pair 1

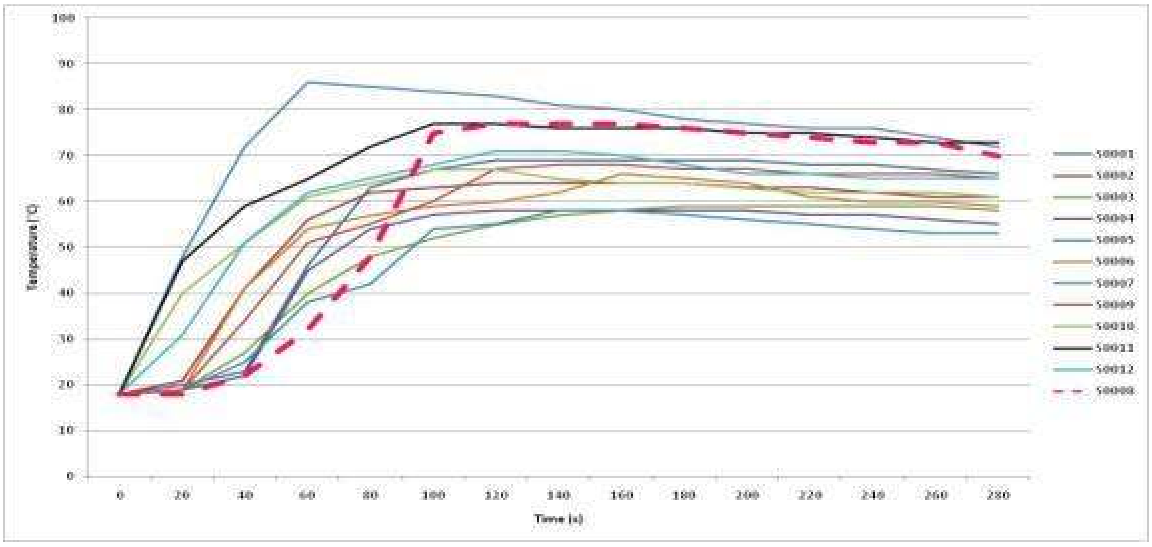


Figure 42 – Reaction Profile of the Pair 1 (First Taguchi Trial Setup)

In general, the increment of the accelerator (Bisomer PTE) in the formulations influences the velocity of the curing process. While in other hand the influence of the initiator (Perkadox CH-50L) is not totally visible, because in some cases the velocity and the temperature of curing have not changed by the fact of using different values of initiator. All samples have registered results with very high speed of curing, another adjustment of the quantity of accelerator and initiator is needed.

Sample	Initiator (pbw)	Accelerator (pbw)
S0013	0.25	0.25
S0014	0.25	0.50
S0015	0.25	0.75
S0016	0.25	2
S0017	0.25	3
S0018	0.25	4
S0019	0.50	0.25
S0020	0.50	1
S0021	0.50	2
S0022	0.50	4

Table 14 – Second Taguchi Trial Setup for the Pair 1

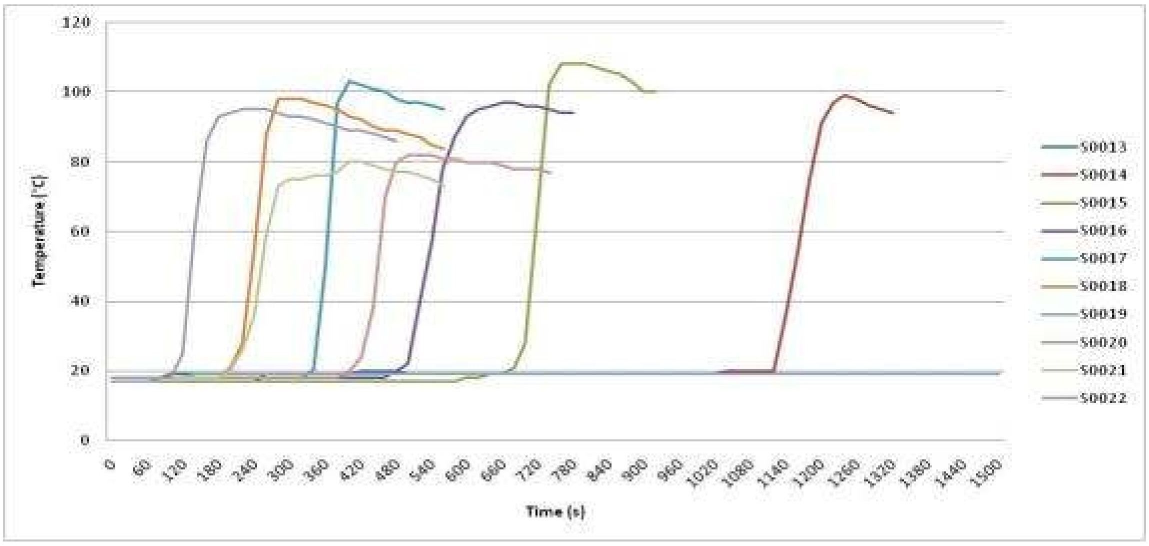


Figure 43 – Reaction Profile of the Pair 1 (Second Taguchi Trial Setup)

The best results were obtained with the samples S0014, S0015, S0016 and S0020. But besides the good results regarding the curing time, the temperature of curing is still too high. Another adjustment of the quantity of accelerator and initiator is needed.

Sample	Initiator (pbw)	Accelerator (pbw)
S0023	1	0,25
S0024	1	0,5
S0025	2	0,5

Table 15 – Third Taguchi Trial Setup for the Pair 1

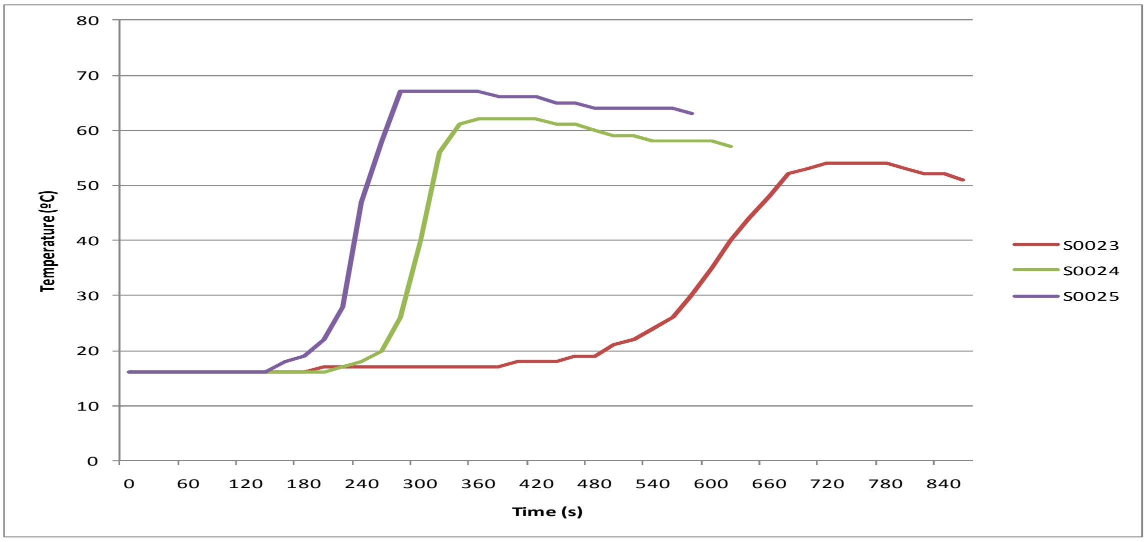


Figure 44 – Reaction Profile of the Pair 1 (Third Taguchi Trial Setup)

The best results were obtained with sample S0023, the desired temperature and time of cure was obtained.

Therefore, the following formulations test will use the combination of the pair initiator/accelerator from the sample S0023.

2.2.1.2 Initiators and Accelerators Comparison

1st Trial – Butanox M50 / Accelerator NL-49 – (Initiator: Accelerator)

Sample	Initiator (pbw)	Accelerator (pbw)
B1	2	2
B2	2	3
B3	2	4

Table 16 – Taguchi Trial Setup for the 1st Trial

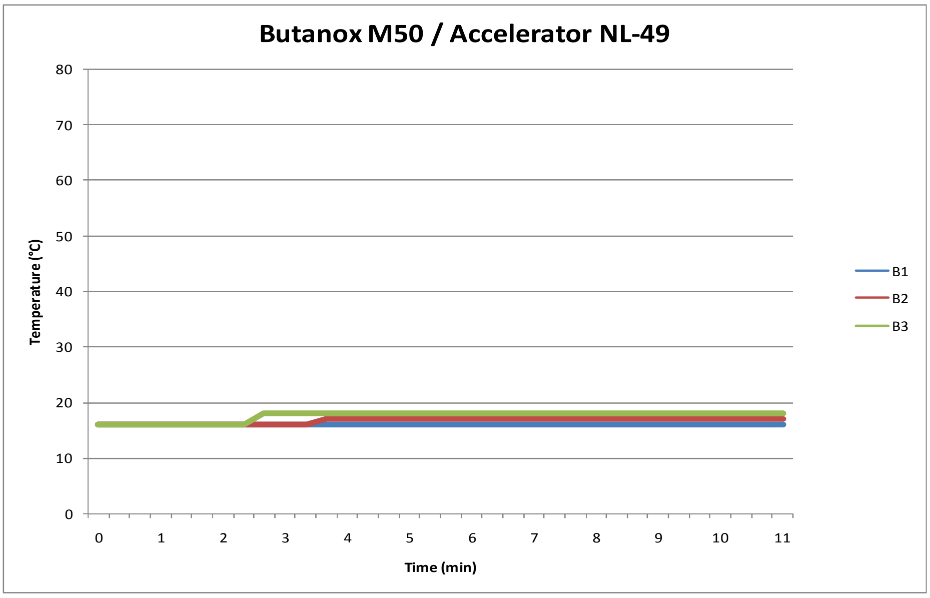


Figure 45 – Reaction Profile of the 1st Trial

2nd Trial – Butanox M50 / Accelerator NL-51 – (Initiator: Accelerator)

Sample	Initiator (pbw)	Accelerator (pbw)
C1	2	1.0
C2	2	1.5
C3	2	2.0

Table 17 – Taguchi Trial Setup for the 2nd Trial

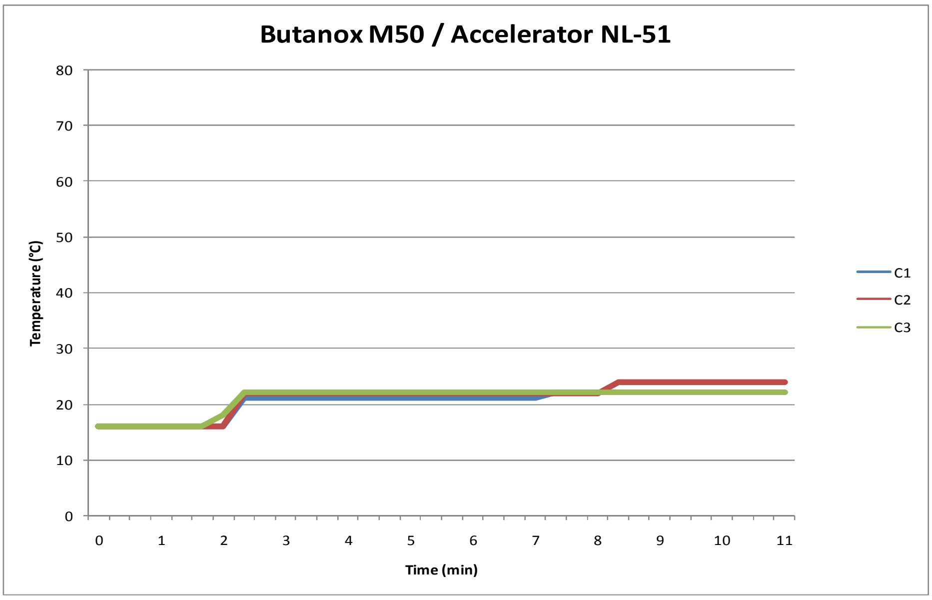


Figure 46 – Reaction Profile of the 2nd Trial

3rd Trial – Butanox P50 / Accelerator NL-49 – (Initiator: Accelerator)

Sample	Initiator (pbw)	Accelerator (pbw)
D1	2	2
D2	2	3
D3	2	4

Table 18 – Taguchi Trial Setup for the 3rd Trial

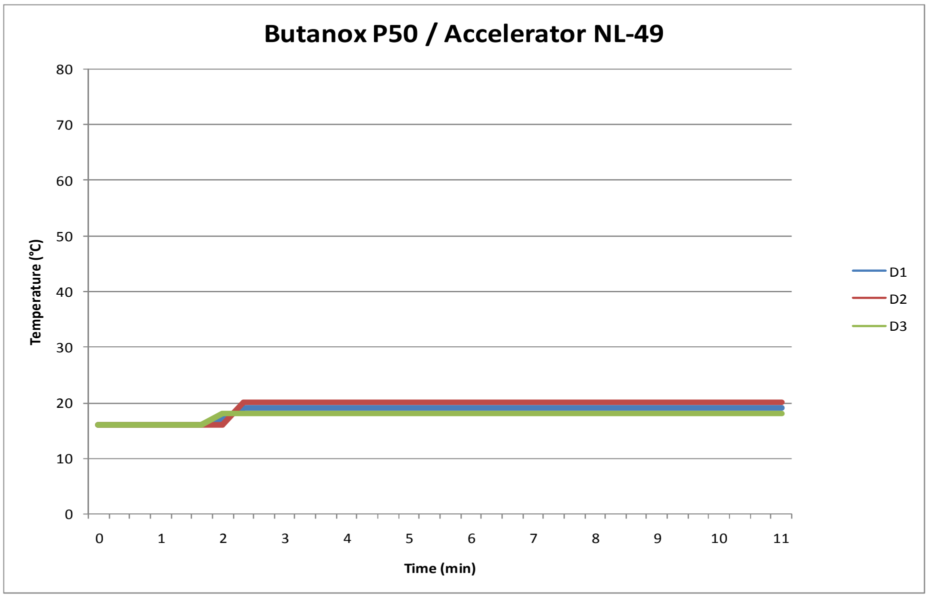


Figure 47 – Reaction Profile of the 3rd Trial

4th Trial – Butanox P50 / Accelerator NL-51 – (Initiator: Accelerator)

Sample	Initiator (pbw)	Accelerator (pbw)
E1	2	2
E2	2	3
E3	2	4

Table 19 – Taguchi Trial Setup for the 4th Trial

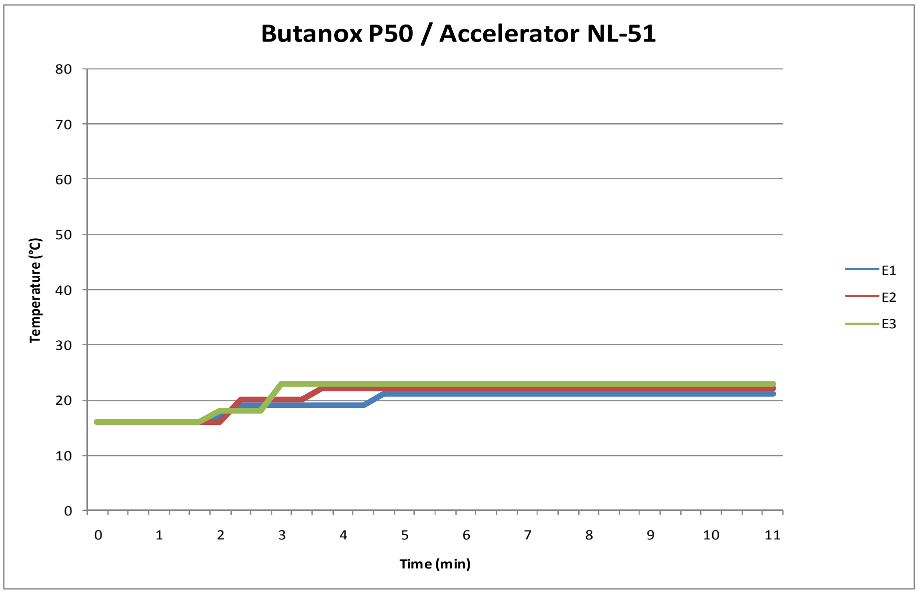


Figure 48 – Reaction Profile of the 4th Trial

5th Trial – Butanox P50 / Accelerator NL-53 – (Initiator: Accelerator)

Sample	Initiator (pbw)	Accelerator (pbw)
F1	2	0.5
F2	2	1.0
F3	2	1.5

Table 20 – Taguchi Trial Setup for the 5th Trial

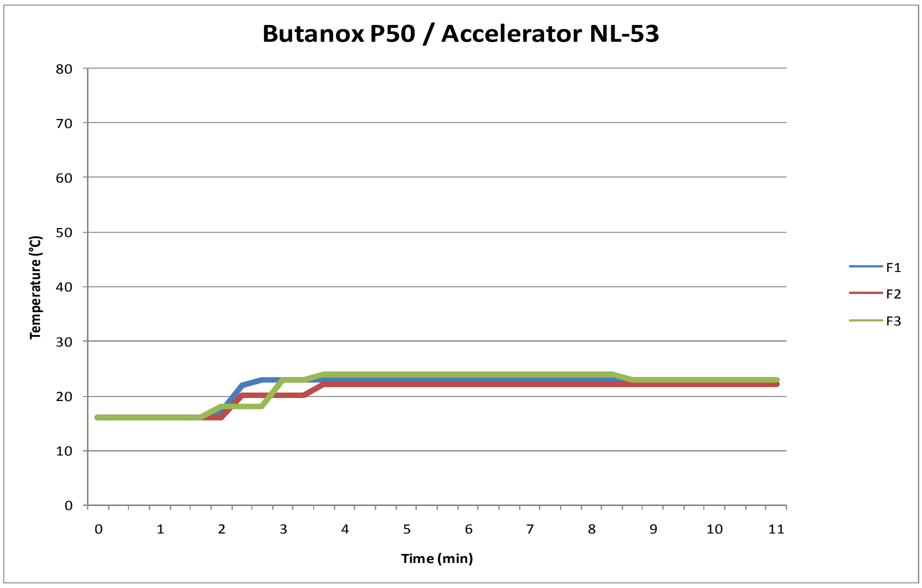


Figure 49 – Reaction Profile of the 5th Trial

All the trials took several days to cure. We can conclude that these systems initiators/accelerators are not suitable for our purposes No further studies will be made based on these pairs.

2.2.1.3 The Influence of the TCPP on the Curing Time and Quality of the Foam

All trials were made with CN9278B80 (trifunctional aliphatic urethane acrylate) combined with the pair initiator/accelerator Perkadox CH-50L and Bisomer PTE.
Different amounts on parts by weight of TCPP were chosen (to a maximum of 60wp) in order to determine if there is any curing process and the time that takes to occur this process.

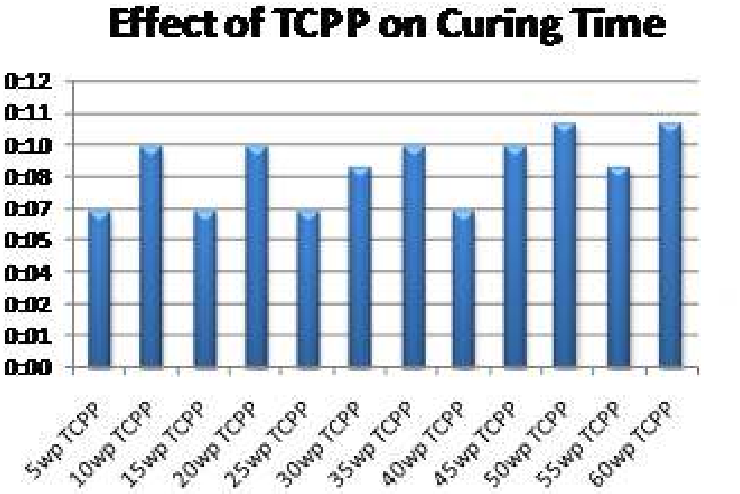


Figure 50 – Curing Time from the different Trials

We can conclude that the addition of TCPP in the mixture have not change the curing time in a significant way but led to outflow and shrinkage of the foams and also to the formation of several bubbles in the trials that used more than 10wp in the mixture. These effects got worse as the amount of TCPP added increased.

2.2.1.4 *Optimization of the Foam*

	Compounds	Parts / weight
Aliphatic Urethane Acrylate	CN 9278B80	85
Crosslinker	PPT1000TMA	15
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	Paraffin	4
Additive	FCA 400	2
Initiator	Perkadox CH-50L	1
Catalyst (Accelerator)	Bisomer PTE	0.25

Table 21 – Formulation A2

The formulation A2 maintains its stability and it’s not sticky. The foam presents a low outflow, a medium flexibility and no brittleness was noticeable. The structure is, at the same time, dense, flexible but is not resilient, characteristics that were difficult to gather in the same foam.

The reaction started after 9:38 minutes (23°C), at the minute 10:00 the temperature was (30°C) and cured at the temperature of 50°C in the 12m50s.

	Compounds	Parts / weight
Aliphatic Urethane Acrylate	CN 9278B80	85
Crosslinker	PPT1000TMA	15
Silicone	B8870	4
Flame retardant	TCPP	8
Additive	Paraffin	4
Additive	FCA 400	7
Initiator	Perkadox CH-50L	1
Catalyst (Accelerator)	Bisomer PTE	0.25

Table 22 – Formulation A3

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The formulation A3 maintain its stability but it’s sticky. Presents a very low outflow, a low flexibility and some base holes. An adjustment in the silicone is needed.

The reaction started after 8:40 minutes (23°C), at the minute 10:00 the temperature was (31°C) and cured at the temperature of 44°C in the minute 11:20.

	Compounds	Parts / weight
Aliphatic Urethane Acrylate	CN 9278B80	85
Crosslinker	PPT1000TMA	15
Silicone	B8870	6
Flame retardant	TCPP	8
Additive	Paraffin	4
Additive	FCA 400	7
Initiator	Perkadox CH-50L	1
Catalyst (Accelerator)	Bisomer PTE	0.25

Table 23 – Formulation A4

The formulation A4 maintains its stability and it’s not sticky. This foam presents a low outflow, a medium flexibility and no shrinkage. The problems of this foam are the glass bubbles, crumbling and cell collapse.

The reaction started after 9:02 minutes (22°C), at the minute 10:00 the temperature was (27°C) and cured at the temperature of 47°C in the minute 12:18.

	Compounds	Parts / weight
Aliphatic Urethane Acrylate	CN 9278B80	85
Crosslinker	PPT1000TMA	15
Silicone	B8870	7
Flame retardant	TCPP	8
Additive	Paraffin	4
Additive	FCA 400	4
Initiator	Perkadox CH-50L	1
Catalyst (Accelerator)	Bisomer PTE	0.25

Table 24 – Formulation A5

In the formulation A5 the amount of silicone seemed to give the right stability to the foam but it´s still sticky. The FCA400 amount should be adjusted to enhance a good mixing.

The reaction started after 9:13 minutes (23°C), at the minute 10:00 the temperature was (33°C) and cured at the temperature of 46°C in the minute 12:02.

	Compounds	Parts / weight
Aliphatic Urethane Acrylate	CN 9278B80	85
Crosslinker	PPT1000TMA	15
Silicone	B8870	7
Flame retardant	TCPP	8
Additive	Paraffin	4
Additive	FCA 400	5
Initiator	Perkadox CH-50L	1
Catalyst (Accelerator)	Bisomer PTE	0.25

Table 25 – Formulation A6

An adjustment of the FCA400 is still needed. The formulation A6 is very similar to the A5. The quality of the foam seems to be promising even though the sticking problems.

The reaction started after 9:22 minutes (23°C), at the minute 10:00 the temperature was (30°C) and cured at the temperature of 47°C in the minute 12:48.

	Compounds	Parts / weight
Aliphatic Urethane Acrylate	CN 9278B80	85
Crosslinker	PPT1000TMA	15
Silicone	B8870	7
Flame retardant	TCPP	8
Additive	Paraffin	4
Additive	FCA 400	6
Initiator	Perkadox CH-50L	1
Catalyst (Accelerator)	Bisomer PTE	0.25

Table 26 – Formulation A7

The formulation A7 gave the best foam results. The external and internal parameters have similarities with the PU Foams and the physical tests gave promising results.

The reaction started after 9:16 minutes (22°C), at the minute 10:00 the temperature was (31°C) and cured at the temperature of 46°C in the minute 12:23.

	Compounds	Parts / weight
Unsaturated Polyester	Synocure 505	85
Crosslinker	PPT1000TMA	15
Silicone	B8870	7
Flame retardant	TCPP	8
Additive	Paraffin	4
Additive	FCA 400	6
Initiator	Perkadox CH-50L	1
Catalyst (Accelerator)	Bisomer PTE	0.25

Table 27 – Formulation A8

Formulation A8 was made to understand the role of the unsaturated polyester as resin. The result was foam with a bad cell structure, very brittle but with an excellent adhesion. No measurements were made to the curing process.

	Compounds	Parts / weight
Aliphatic Urethane Acrylate	CN 9278B80	42,5
Unsaturated Polyester	Synocure 505	42,5
Crosslinker	PPT1000TMA	15
Silicone	B8870	7
Flame retardant	TCPP	8
Additive	Paraffin	4
Additive	FCA 400	6
Initiator	Perkadox CH-50L	1
Catalyst (Accelerator)	Bisomer PTE	0.25

Table 28 – Formulation A9

The formulation A9 gave a very rigid structure with low density and a bad cell structure. An adjustment on the ratio of Synocure 505 and CN9278B80 is needed.

The reaction started after 8:10 minutes (23°C), at the minute 10:00 the temperature was (39°C) and cured at the temperature of 55°C in the minute 11:20.

	Compounds	Parts / weight
Aliphatic Urethane Acrylate	CN 9278B80	73
Unsaturated Polyester	Synocure 505	12
Crosslinker	PPT1000TMA	15
Silicone	B8870	7
Flame retardant	TCPP	8
Additive	Paraffin	4
Additive	FCA 400	6
Initiator	Perkadox CH-50L	1
Catalyst (Accelerator)	Bisomer PTE	0.25

Table 29 – Formulation A10

The unsaturated polyester besides giving good results at the adhesion, is giving a structure very rigid. The density values are low. An adjustment on the Synocure 505 ratio is needed.

The reaction started after 8:40 minutes (22°C), at the minute 10:00 the temperature was (36°C) and cured at the temperature of 41°C in the minute 11:57.

	Compounds	Parts / weight
Aliphatic Urethane Acrylate	CN 9278B80	77
Unsaturated Polyester	Synocure 505	8
Crosslinker	PPT1000TMA	15
Silicone	B8870	7
Flame retardant	TCPP	8
Additive	Paraffin	4
Additive	FCA 400	6
Initiator	Perkadox CH-50L	1
Catalyst (Accelerator)	Bisomer PTE	0.25

Table 30 – Formulation A11

The formulation A11 needs again an adjustment on the Synocure 505 ratio. The use of unsaturated polyester is not giving good results besides the adhesion. A last trial should be gone with the Synocure 505 in order to determinate if will be used in a future base formulation.

The reaction started after 8:52 minutes (23°C), at the minute 10:00 the temperature was (34°C) and cured at the temperature of 49°C in the minute 12:02.

	Compounds	Parts / weight
Aliphatic Urethane Acrylate	CN 9278B80	81
Unsaturated Polyester	Synocure 505	4
Crosslinker	PPT1000TMA	15
Silicone	B8870	7
Flame retardant	TCPP	8
Additive	Paraffin	4
Additive	FCA 400	6
Initiator	Perkadox CH-50L	1
Catalyst (Accelerator)	Bisomer PTE	0.25

Table 31 – Formulation A12

All the formulations using the unsaturated polyester resin (Synocure 505) gave foams with low density´s, very rigid and with a bad cell structures. No studies will further be made on this type of resin.

The reaction started after 8:42 minutes (23°C), at the minute 10:00 the temperature was (35°C) and cured at the temperature of 50°C in the minute 11:22.

	Compounds	Parts / weight
Aliphatic Urethane Acrylate	CN 9278B80	90
Crosslinker	PPT1000TMA	10
Silicone	B8870	7
Flame retardant	TCPP	8
Additive	Paraffin	4
Additive	FCA 400	6
Initiator	Perkadox CH-50L	1
Catalyst (Accelerator)	Bisomer PTE	0.25

Table 32 – Formulation A13

The foam obtained with the formulation A13 gave good mechanical and structural results besides the high viscosity of the formulation. The density values are high. The formulation A7 is still the best so far.

The reaction started after 9:54 minutes (23°C), at the minute 10:00 the temperature was (26°C) and cured at the temperature of 46°C in the minute 12:42.

	Compounds	Parts / weight
Aliphatic Urethane Acrylate	CN 9278B80	100
Silicone	B8870	7
Flame retardant	TCPP	8
Additive	Paraffin	4
Additive	FCA 400	6
Initiator	Perkadox CH-50L	1
Catalyst (Accelerator)	Bisomer PTE	0.25

Table 33 – Formulation A14

The viscosity of the formation A14 is very high. Only a small amount of foam is dispensed. The use of PPT1000TMA as crosslinker is essential to acquire the right viscosity. The formulation A7 seems to be the one with the right ratio composition.
The reaction started after 9:48 minutes (22°C), at the minute 10:00 the temperature was (25°C) and cured at the temperature of 48°C in the minute 13:10.

	Compounds	Parts / weight
Aromatic Urethane Acrylate	PRO 20652	85
Crosslinker	PPT1000TMA	15
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	Paraffin	4
Additive	FCA 400	6
Initiator	Perkadox CH-50L	1
Catalyst (Accelerator)	Bisomer PTE	0.25

Table 34 – Formulation A15

The formulation A15 was made to view the foam structure using an aromatic urethane acrylate as resin. The resin PRO 20652 is not commercialized yet as the material available was just a sample of the product it was not possible to do more formulations. This formulation gave similar results to the aliphatic version regarding the structural view, but gave worst results about the mechanical properties
The reaction started after 9:40 minutes (22°C), at the minute 10:00 the temperature was (27°C) and cured at the temperature of 42°C in the minute 12:04s.

2.2.2 Route 2

2.2.2.1 Optimizing Viscosity for Spraying

The initial work was dedicated to the study of the availability of the necessary chemicals. The main problem is to obtain NCO-terminated prepolymer being simultaneously liquid, with low viscosity for spraying and to complete the monomers successfully in view of obtaining foam with good characteristics.

- **Prepolymer 1**

Prepolymer 1	
Compounds	**Parts / weight**
Suprasec 2004	48,1
Ethyl Hexanol	7,2
Castor Oil	16,6
2-HEA	28,2
PEG1000TMA	16

Table 35 – Formulation of Prepolymer 1

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 1	84
Crosslinker	PPT1000TMA	16
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	0,5

Table 36 – Formulation P1

This formulation presents a very high viscosity and cannot spray. An adjustment on the compounds ratio of the prepolymer 1 is needed.

- **Prepolymer 2**

Prepolymer 2	
Compounds	**Parts / weight**
Suprasec 2004	36,83
Ethyl Hexanol	4,95
Castor Oil	12,68
2-HEA	20,47
PEG1000TMA	17,6

Table 37 – Formulation of Prepolymer 2

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 2	75
Active Diluent	2-HEA	8,9
Crosslinker	PPT1000TMA	17,6
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	0,5

Table 38 – Formulation P2

The prepolymer P2 regarding the P1 has lower viscosity due to the use of an active diluent on the formulation and can be sprayed. The result was bad homogeneity of the foam and bad adhesion on the paper. Maybe some separation occurred and some components stayed in the can.

- **Prepolymer 3**

Prepolymer 3	
Compounds	**Parts / weight**
Suprasec 2004	32,7
Rokopol 1002D	15,9
Rokopol GT500	7,8
2-HEA	15,1
PEG1000TMA	30

Table 39 – Formulation of Prepolymer 3

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 3	71,5
Crosslinker	PPT1000TMA	30
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	0,5

Table 40 – Formulation P3

The formulation P3 had an excellent viscosity and an excellent shaking rate. The foam P3 instead presented very bad results, the foam was too flexible, had a bad spraying and a very slow cure.

- **Prepolymer 4**

Prepolymer 4	
Compounds	**Parts / weight**
Suprasec 2004	15,6
Rokopol 1002D	32,1
SR604	33,6
SR610	18,7

Table 41 – Formulation of Prepolymer 4

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 4	100
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	0,5

Table 42 – Formulation P4

The formulation P4 presents good viscosity. The foam had a satisfactory spray but the foam is still too flexible and the toughness is missing.

- **Prepolymer 5**

Prepolymer 5	
Compounds	**Parts / weight**
Suprasec 2004	15,6
Rokopol 1002D	32,1
SR604	33,6
SR610	12,4
SR9020	6,3

Table 43 – Formulation of Prepolymer 5

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 5	100
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	0,5

Table 44 – Formulation P5

No progresses were made with the formulation P5 in comparison with P4. The influence of SR9020 is not visible and the results were the same as in the formulation P4.

- **Prepolymer 6**

Prepolymer 6	
Compounds	**Parts / weight**
Suprasec 2004	21,8
Rokopol G1000	30,4
SR604	15,8
SR238	17
PEG1000TMA	15

Table 45 – Formulation of Prepolymer 6

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 6	100
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	0,5

Table 46 – Formulation P6

This formulation P6 failed to spray. The viscosity of the prepolymer 6 is very high.

- **Prepolymer 7**

Prepolymer 7	
Compounds	**Parts / weight**
Suprasec 2004	30,9
Rokopol GT500	21,3
2-HEA	17
SR238	15,7
PEG1000TMA	15

Table 47 – Formulation of Prepolymer 7

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 7	100
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	2

Table 48 – Formulation P7

This foam cannot spray because there was gelation inside the can. Probably some separation occurred inside the can.

- **Prepolymer 8**

Prepolymer 8	
Compounds	**Parts / weight**
Suprasec 2004	17,4
Rokopol GT500	12,5
SR604	38,1
SR238	17
PEG1000TMA	15

Table 49 – Formulation of Prepolymer 8

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 8	100
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	1,5

Table 50 – Formulation P8

In this formulation the spraying process was very good, the foam presented a good homogeneity and there was adhesion on the paper. The toughness problem still persists and some shrinkage after curing was noticed.

- **Prepolymer 9**

Prepolymer 9	
Compounds	**Parts / weight**
Suprasec 2004	21,9
Rokopol GT500	15,5
SR604	33,9
SR238	18
PEG1000TMA	10

Table 51 – Formulation of Prepolymer 9

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 9	100
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	2

Table 52 – Formulation P9

The results were very similar to the formulation P8. The problem of flexibility and lack of toughness still persists.

- **Prepolymer 10**

Prepolymer 10	
Compounds	**Parts / weight**
Suprasec 2004	44,6
Glycerin	5,5
2-HEA	21,9
SR238	18
SR9020	10

Table 53 – Formulation of Prepolymer 10

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 10	100
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	1,5

Table 54 – Formulation P10

This formulation had good viscosity but failed to spray, there was an obvious separation inside the can.

- **Prepolymer 11**

Prepolymer 11	
Compounds	**Parts / weight**
Suprasec 2004	21,3
Glycerin	2,6
SR604	36,1
SR238	20
SR9020	20

Table 55 – Formulation of Prepolymer 11

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 11	100
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	1,5

Table 56 – Formulation P11

The formulation P11 failed to spray although having good viscosity of the prepolymer P11. The conclusion was that the bigger part of prepolymer presented separation by sedimentation when filling with gas.

- **Prepolymer 12**

Prepolymer 12	
Compounds	**Parts / weight**
Suprasec 2004	27,5
2-HEA	13
SR604	39,5
SR238	20

Table 57 – Formulation of Prepolymer 12

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 12	80
Active Diluent	SR9020	20
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	1,5

Table 58 – Formulation P12

The prepolymer P12 presents a very high viscosity in which the spray process is affected. Only a small amount of foam is dispensed.

- **Prepolymer 13**

Prepolymer 13	
Compounds	**Parts / weight**
Suprasec 2004	27
MMA	11,3
SR604	41,7
SR238	20

Table 59 – Formulation of Prepolymer 13

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 13	85
Active Diluent	SR604	3
Active Diluent	SR9020	15
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	1,5

Table 60 – Formulation P13

The prepolymer P12 presents a very good viscosity. The foam after being sprayed collapses and becomes liquid after few minutes.

- **Prepolymer 14**

Prepolymer 14	
Compounds	**Parts / weight**
Suprasec 2004	39,5
Glycerin	4,7
2-HEA	17,6
SR238	18,2
SR9020	20

Table 61 – Formulation of Prepolymer 14

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 14	100
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	1,5

Table 62 – Formulation P14

The formulation P14 cannot spray. There was gelation inside the can due to a very fast curing time.

- **Prepolymer 15**

Prepolymer 15	
Compounds	**Parts / weight**
Suprasec 2004	37,3
Glycerin	4,5
2-HEA	18,3
SR238	16
MMA	9
SR9020	15

Table 63 – Formulation of Prepolymer 15

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 15	100
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	1,5

Table 64 – Formulation P15

This formulation has good spraying due to the good viscosity of the prepolymer P15. The foam had homogeneity, there was adhesion on the paper and there was no shrinkage. As disadvantages this foam was too flexible and presented a poor toughness.

- **Prepolymer 16**

Prepolymer 16	
Compounds	**Parts / weight**
Suprasec 2004	28,3
Glycerin	2,6
MMA	10
SR238	25
SR604	34,1

Table 65 – Formulation of the Prepolymer 16

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 16	100
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	1,5

Table 66 – Formulation P16

The prepolymer P16 presents a medium viscosity which doesn’t affect the spraying process. The foam obtained had homogeneity in the spray but after some minutes some parts of the foam reveal shrinkage. The viscosity of the prepolymer must be lower in order to guarantee a complete homogeneous mixture.

- **Prepolymer 17**

Prepolymer 17	
Compounds	**Parts / weight**
Suprasec 2004	25
Glycerin	3,9
SR238	17,6
SR604	41,5
SR9020	12

Table 67 – Formulation of Prepolymer 17

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 17	100
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	1,5

Table 68 – Formulation P17

This formulation was made on the base of CN927B80. The results were very satisfactory besides the fact of the viscosity was still too high and the spraying process was affected.

- **Prepolymer 18**

Prepolymer 18	
Compounds	**Parts / weight**
Suprasec 2004	21,3
Glycerin	2,6
SR238	20
SR604	36,1
SR9020	20

Table 69 – Formulation of Prepolymer 18

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 18	100
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	1,5

Table 70 – Formulation P18

In this formulation P18 the use of active diluents was increased in comparison with the formulation P17. This result the spraying process was not affected and the foam seems to give promising results.

- **Prepolymer 19**

Prepolymer 19	
Compounds	**Parts / weight**
Suprasec 2004	36,5
Glycerin	4,4
MMA	9
SR238	15,5
2-HEA	19,1
SR9020	15,5

Table 71 – Formulation of Prepolymer 19

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 19	100
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	1,5

Table 72 – Formulation P19

The viscosity of the prepolymer is very high which doesn't permit the dispensing of the foam.

- **Prepolymer 20**

Prepolymer 20	
Compounds	**Parts / weight**
Suprasec 2004	31,7
Rokopol GT500	18,8
MMA	3
SR238	13,4
2-HEA	13,1
SR9020	20

Table 73 – Formulation of Prepolymer 20

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 20	100
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	1,5

Table 74 – Formulation P20

The formulation P20 failed to spray. The viscosity of the prepolymer 20 is good but some separation occurs inside the can.

- **Prepolymer 21**

Prepolymer 21	
Compounds	**Parts / weight**
Suprasec 2004	43
Glycerin	4,8
MMA	3
SR238	11,6
2-HEA	17,6
SR9020	20

Table 75 – Formulation of Prepolymer 21

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 21	100
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	1,5

Table 76 – Formulation P21

The formulation P21 failed to spray. The viscosity of the prepolymer seemed to be fine but some gelation happened inside the can. Maybe the effects of the moisture are affecting the prepolymer shelf life.

- **Prepolymer 22**

Prepolymer 22	
Compounds	**Parts / weight**
Suprasec 2004	32,8
Glycerin	3,9
SR495B	43,3
SR238	20

Table 77 – Formulation of Prepolymer 22

	Compounds	Parts / weight
Acrylic Terminated Prepolymer	Prepolymer 21	100
Silicone	B8870	1
Flame retardant	TCPP	8
Additive	FCA 400	2
Initiator	Perkadox CH-50L	4
Catalyst (Accelerator)	Bisomer PTE	1,5

Table 78 – Formulation P22

The formulation P22 failed to spray due to high viscosity of the prepolymer 22.

2.2.2.2 Optimizing Composition to Give Appropriate Foam

Formulation	Compounds	Details of the Variations
B1	80% MFUA – 20% BFUA	-
B2	100% TFUA	-
B3	80% TFUA – 20% MFUA	-
B4	50% TFUA – 33,7% MFUA – 16,3% BFUA	-
B5	40% TFUA – 39,3% MFUA – 20,7% BFUA	-
B6	60% TFUA – 26,2% MFUA – 13,8% BFUA	-
B7	30% TFUA – 45,9% MFUA – 24,1% BFUA	-
B8	60% TFUA – 20% MFUA – 20% BFUA	-
B8A*	60% TFUA – 20% MFUA – 20% BFUA	1/3 of the total LPG and DME used
B8B*	60% TFUA – 20% MFUA – 20% BFUA	2/3 of the total LPG and DME used
B8C*	60% TFUA – 20% MFUA – 20% BFUA	1/2 of the total LPG and DME used
B8D*	60% TFUA – 20% MFUA – 20% BFUA	No DME used
B8E*	60% TFUA – 20% MFUA – 20% BFUA	No paraffin used
B8F*	60% TFUA – 20% MFUA – 20% BFUA	1/2 of the FCA400 and B8870 used
B8G*	60% TFUA – 20% MFUA – 20% BFUA	2/3 of the total GAS, 1/2 of the FCA400 and B8870 used

Table 79 – Order of Formulations

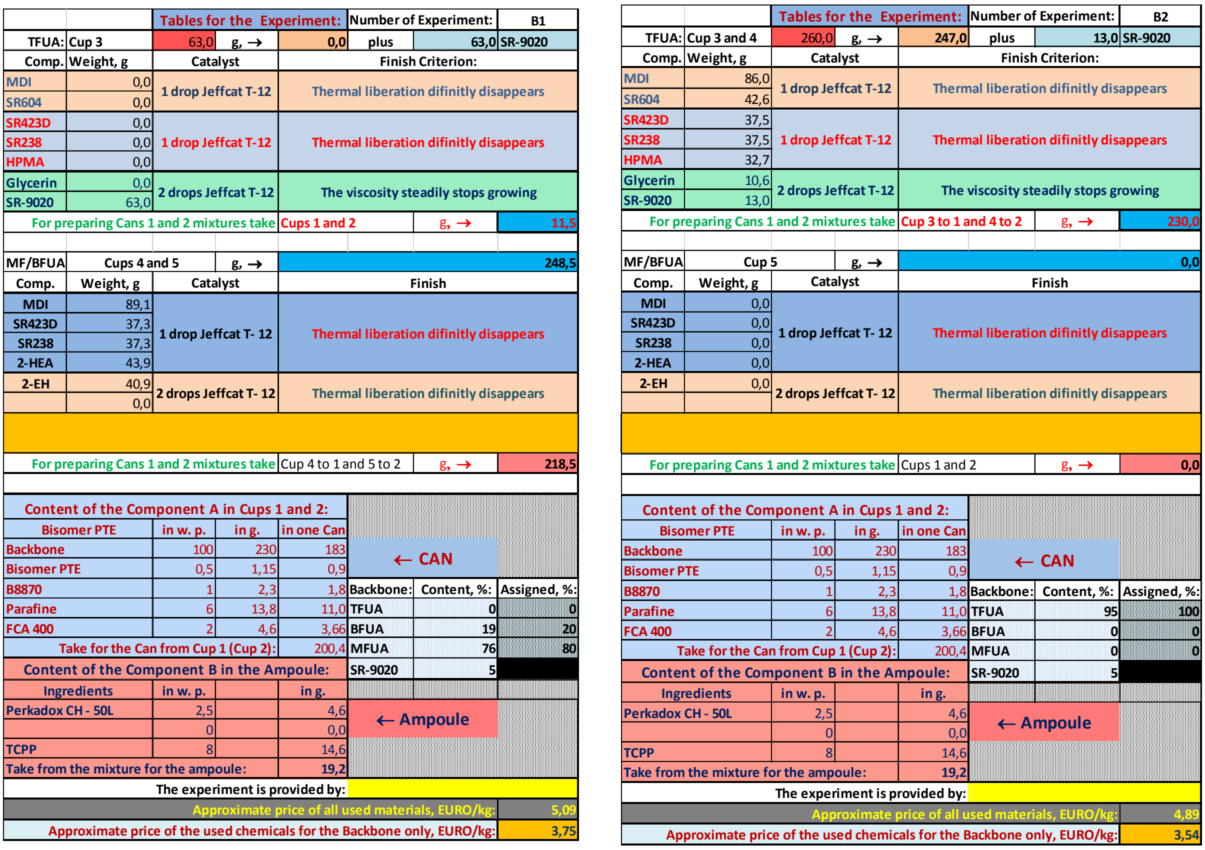
*** -** Variations of the formulation B8

All the formulations for optimizing composition to give the appropriate foam where made using a model for calculation by percentage of each functionality developed in Altachem NV, this model is demonstrated in the figures 51,52,53 and 54.

The B1, B2 and B3 formulations were made to understand the role of each functionality on the engineering of the backbone, these foams presented big expansion after spraying but after several minutes some shrinkage was observed.

The formulations B4, B5, B6 and B7 gave foams where we took some good conclusions but the formulation B8 besides having a very good structure obtained the best results in the density measurements and physical tests. So regarding the objectives of this project, this was the formulation that we chose for starting our research, this formulation has several good properties that can be tune-up in order to obtain a final foam with similar properties of the PU foams. The variation that obtained the best results is the formulation B8G.

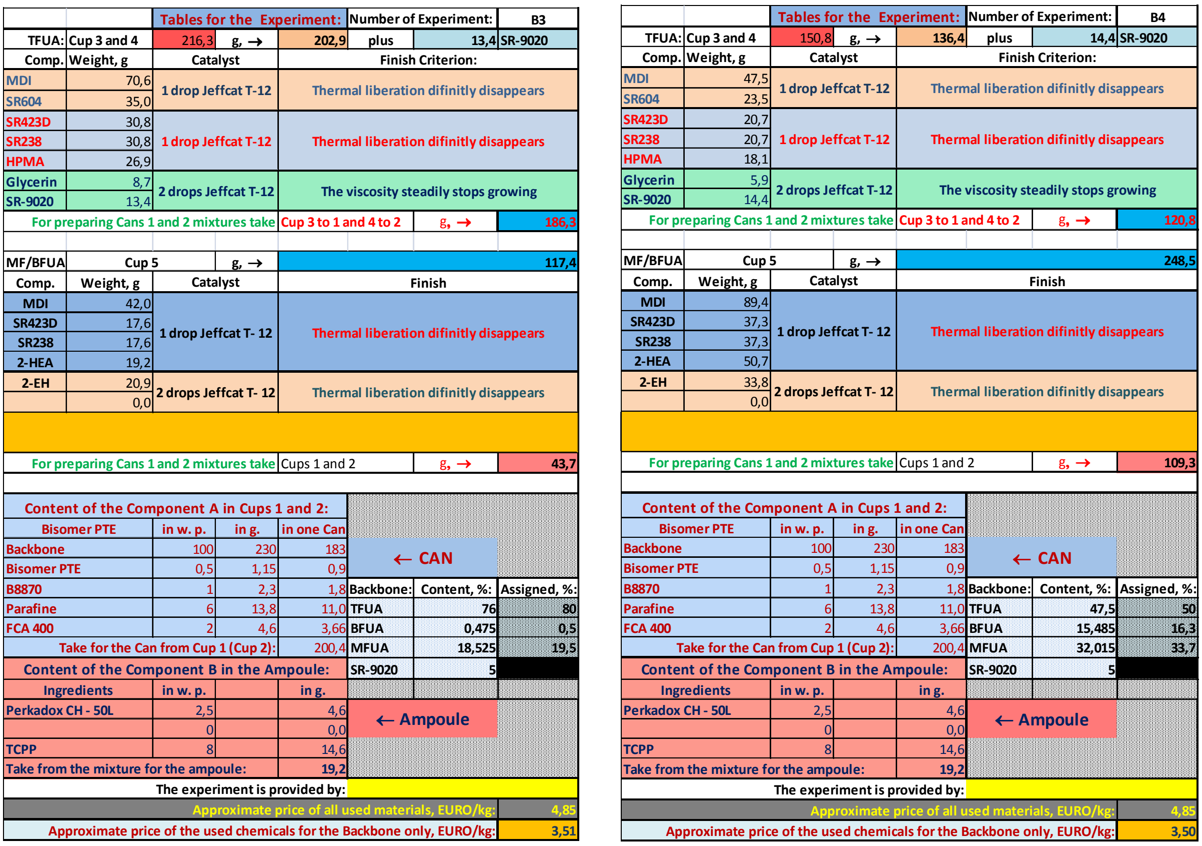
From the different foam trials made with these backbones we can conclude that regarding to the gas is possible to vary the ODM with small variations of volume of gas and if we use only ½ of volume gas by mixture than the can cannot be totally dispended. Regarding to paraffin we discovered that besides reducing the shrinkage it also increases the density values.



		Tables for the Experiment:			Number of Experiment:		B1
TFUA:	Cup 3	63,0	g, →	0,0	plus	63,0	SR-9020
Comp.	Weight, g	Catalyst		Finish Criterion:			
MDI	0,0	1 drop Jeffcat T-12		Thermal liberation difinitly disappears			
SR604	0,0						
SR423D	0,0	1 drop Jeffcat T-12		Thermal liberation difinitly disappears			
SR238	0,0						
HPMA	0,0						
Glycerin	0,0	2 drops Jeffcat T-12		The viscosity steadily stops growing			
SR-9020	63,0						
For preparing Cans 1 and 2 mixtures take				Cups 1 and 2		g, →	11,5
MF/BFUA	Cups 4 and 5		g, →	248,5			
Comp.	Weight, g	Catalyst		Finish			
MDI	89,1	1 drop Jeffcat T- 12		Thermal liberation difinitly disappears			
SR423D	37,3						
SR238	37,3						
2-HEA	43,9						
2-EH	40,9	2 drops Jeffcat T- 12		Thermal liberation difinitly disappears			
	0,0						
For preparing Cans 1 and 2 mixtures take				Cup 4 to 1 and 5 to 2		g, →	218,5
Content of the Component A in Cups 1 and 2:							
Bisomer PTE		in w. p.	in g.	in one Can			
Backbone		100	230	183	← CAN		
Bisomer PTE		0,5	1,15	0,9			
B8870		1	2,3	1,8	Backbone:	Content, %:	Assigned, %:
Parafine		6	13,8	11,0	TFUA	0	0
FCA 400		2	4,6	3,66	BFUA	19	20
Take for the Can from Cup 1 (Cup 2):				200,4	MFUA	76	80
Content of the Component B in the Ampoule:					SR-9020	5	
Ingredients		in w. p.		in g.			
Perkadox CH - 50L		2,5		4,6	← Ampoule		
		0		0,0			
TCPP		8		14,6			
Take from the mixture for the ampoule:				19,2			
The experiment is provided by:							
Approximate price of all used materials, EURO/kg:							5,09
Approximate price of the used chemicals for the Backbone only, EURO/kg:							3,75

		Tables for the Experiment:			Number of Experiment:		B2
TFUA:	Cup 3 and 4	260,0	g, →	247,0	plus	13,0	SR-9020
Comp.	Weight, g	Catalyst		Finish Criterion:			
MDI	86,0	1 drop Jeffcat T-12		Thermal liberation difinitly disappears			
SR604	42,6						
SR423D	37,5	1 drop Jeffcat T-12		Thermal liberation difinitly disappears			
SR238	37,5						
HPMA	32,7						
Glycerin	10,6	2 drops Jeffcat T-12		The viscosity steadily stops growing			
SR-9020	13,0						
For preparing Cans 1 and 2 mixtures take				Cup 3 to 1 and 4 to 2		g, →	230,0
MF/BFUA	Cup 5		g, →	0,0			
Comp.	Weight, g	Catalyst		Finish			
MDI	0,0	1 drop Jeffcat T- 12		Thermal liberation difinitly disappears			
SR423D	0,0						
SR238	0,0						
2-HEA	0,0						
2-EH	0,0	2 drops Jeffcat T- 12		Thermal liberation difinitly disappears			
For preparing Cans 1 and 2 mixtures take				Cups 1 and 2		g, →	0,0
Content of the Component A in Cups 1 and 2:							
Bisomer PTE		in w. p.	in g.	in one Can			
Backbone		100	230	183	← CAN		
Bisomer PTE		0,5	1,15	0,9			
B8870		1	2,3	1,8	Backbone:	Content, %:	Assigned, %:
Parafine		6	13,8	11,0	TFUA	95	100
FCA 400		2	4,6	3,66	BFUA	0	0
Take for the Can from Cup 1 (Cup 2):				200,4	MFUA	0	0
Content of the Component B in the Ampoule:					SR-9020	5	
Ingredients		in w. p.		in g.			
Perkadox CH - 50L		2,5		4,6	← Ampoule		
		0		0,0			
TCPP		8		14,6			
Take from the mixture for the ampoule:				19,2			
The experiment is provided by:							
Approximate price of all used materials, EURO/kg:							4,89
Approximate price of the used chemicals for the Backbone only, EURO/kg:							3,54

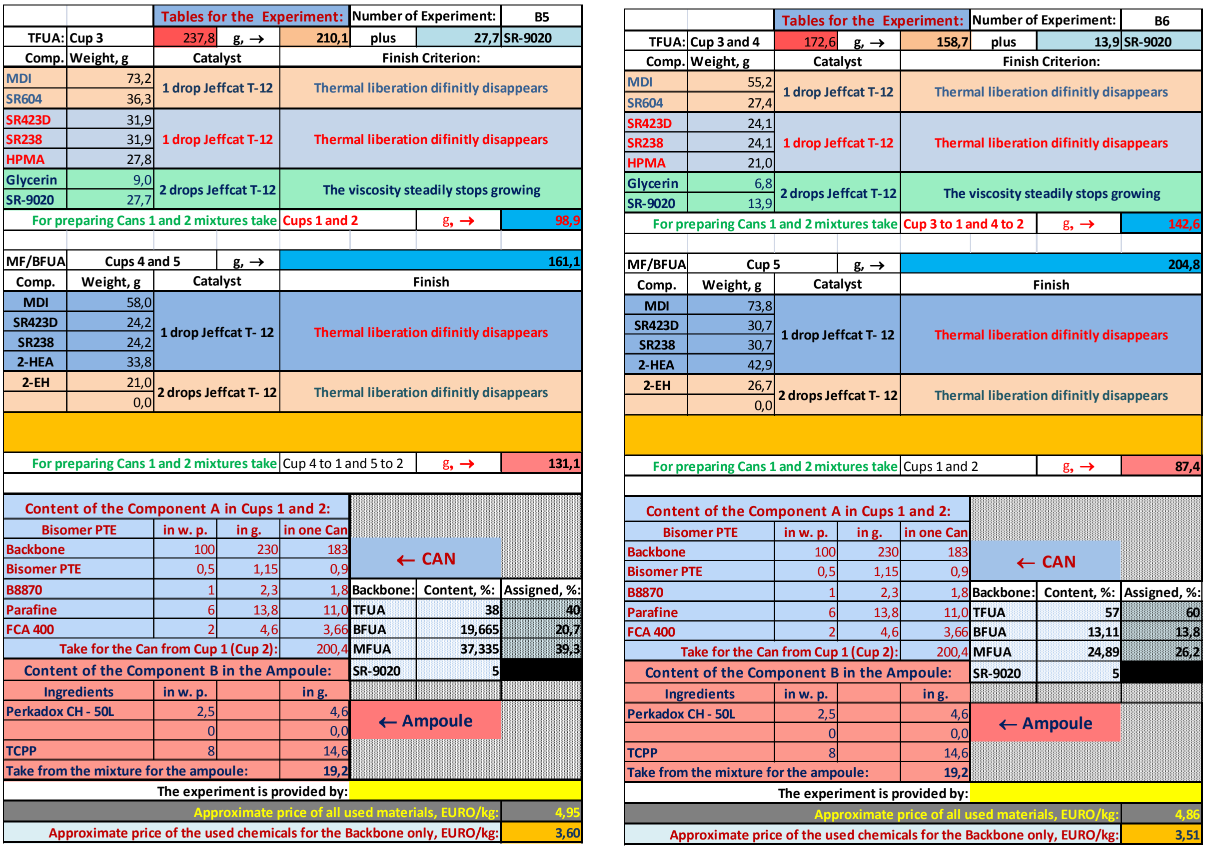
Figure 51 – Formulations B1 and B2



		Tables for the Experiment:			Number of Experiment:		B3
TFUA:	Cup 3 and 4	216,3	g, →	202,9	plus	13,4	SR-9020
Comp.	Weight, g	Catalyst		Finish Criterion:			
MDI	70,6	1 drop Jeffcat T-12		Thermal liberation difinitly disappears			
SR604	35,0						
SR423D	30,8	1 drop Jeffcat T-12		Thermal liberation difinitly disappears			
SR238	30,8						
HPMA	26,9						
Glycerin	8,7	2 drops Jeffcat T-12		The viscosity steadily stops growing			
SR-9020	13,4						
For preparing Cans 1 and 2 mixtures take				Cup 3 to 1 and 4 to 2		g, →	186,3
MF/BFUA	Cup 5		g, →	117,4			
Comp.	Weight, g	Catalyst		Finish			
MDI	42,0	1 drop Jeffcat T- 12		Thermal liberation difinitly disappears			
SR423D	17,6						
SR238	17,6						
2-HEA	19,2						
2-EH	20,9	2 drops Jeffcat T- 12		Thermal liberation difinitly disappears			
	0,0						
For preparing Cans 1 and 2 mixtures take				Cups 1 and 2		g, →	43,7
Content of the Component A in Cups 1 and 2:							
Bisomer PTE		in w. p.	in g.	in one Can			
Backbone		100	230	183	← CAN		
Bisomer PTE		0,5	1,15	0,9			
B8870		1	2,3	1,8	Backbone:	Content, %:	Assigned, %:
Parafine		6	13,8	11,0	TFUA	76	80
FCA 400		2	4,6	3,66	BFUA	0,475	0,5
Take for the Can from Cup 1 (Cup 2):				200,4	MFUA	18,525	19,5
Content of the Component B in the Ampoule:					SR-9020	5	
Ingredients		in w. p.		in g.			
Perkadox CH - 50L		2,5		4,6	← Ampoule		
		0		0,0			
TCPP		8		14,6			
Take from the mixture for the ampoule:				19,2			
The experiment is provided by:							
Approximate price of all used materials, EURO/kg:							4,85
Approximate price of the used chemicals for the Backbone only, EURO/kg:							3,51

		Tables for the Experiment:			Number of Experiment:		B4
TFUA:	Cup 3 and 4	150,8	g, →	136,4	plus	14,4	SR-9020
Comp.	Weight, g	Catalyst		Finish Criterion:			
MDI	47,5	1 drop Jeffcat T-12		Thermal liberation difinitly disappears			
SR604	23,5						
SR423D	20,7	1 drop Jeffcat T-12		Thermal liberation difinitly disappears			
SR238	20,7						
HPMA	18,1						
Glycerin	5,9	2 drops Jeffcat T-12		The viscosity steadily stops growing			
SR-9020	14,4						
For preparing Cans 1 and 2 mixtures take				Cup 3 to 1 and 4 to 2		g, →	120,8
MF/BFUA	Cup 5		g, →	248,5			
Comp.	Weight, g	Catalyst		Finish			
MDI	89,4	1 drop Jeffcat T- 12		Thermal liberation difinitly disappears			
SR423D	37,3						
SR238	37,3						
2-HEA	50,7						
2-EH	33,8	2 drops Jeffcat T- 12		Thermal liberation difinitly disappears			
	0,0						
For preparing Cans 1 and 2 mixtures take				Cups 1 and 2		g, →	109,3
Content of the Component A in Cups 1 and 2:							
Bisomer PTE		in w. p.	in g.	in one Can			
Backbone		100	230	183	← CAN		
Bisomer PTE		0,5	1,15	0,9			
B8870		1	2,3	1,8	Backbone:	Content, %:	Assigned, %:
Parafine		6	13,8	11,0	TFUA	47,5	50
FCA 400		2	4,6	3,66	BFUA	15,485	16,3
Take for the Can from Cup 1 (Cup 2):				200,4	MFUA	32,015	33,7
Content of the Component B in the Ampoule:					SR-9020	5	
Ingredients		in w. p.		in g.			
Perkadox CH - 50L		2,5		4,6	← Ampoule		
		0		0,0			
TCPP		8		14,6			
Take from the mixture for the ampoule:				19,2			
The experiment is provided by:							
Approximate price of all used materials, EURO/kg:							4,85
Approximate price of the used chemicals for the Backbone only, EURO/kg:							3,50

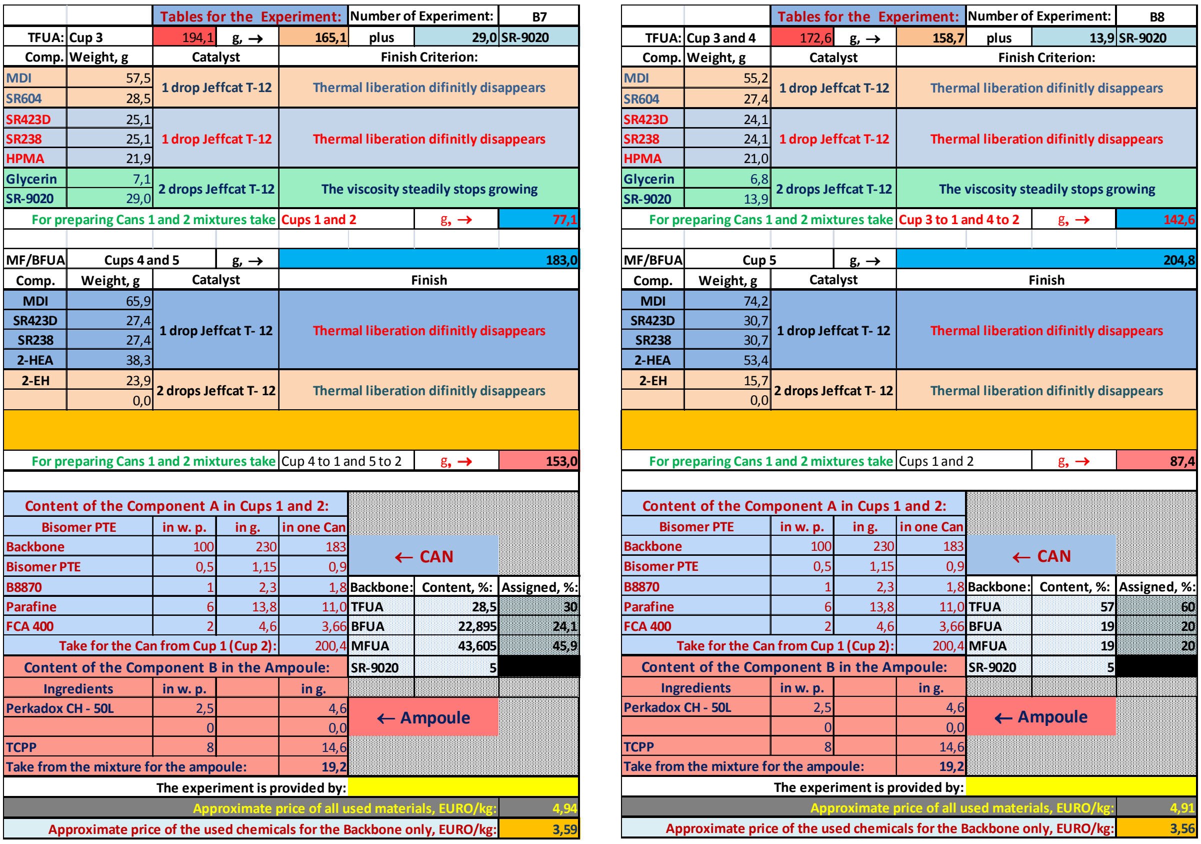
Figure 52 – Formulations B3 and B4



		Tables for the Experiment:			Number of Experiment:		B5
TFUA:	Cup 3	237,8	g, →	210,1	plus	27,7	SR-9020
Comp.	Weight, g	Catalyst		Finish Criterion:			
MDI	73,2	1 drop Jeffcat T-12		Thermal liberation difinitly disappears			
SR604	36,3						
SR423D	31,9	1 drop Jeffcat T-12		Thermal liberation difinitly disappears			
SR238	31,9						
HPMA	27,8						
Glycerin	9,0	2 drops Jeffcat T-12		The viscosity steadily stops growing			
SR-9020	27,7						
For preparing Cans 1 and 2 mixtures take				Cups 1 and 2		g, →	98,9
MF/BFUA	Cups 4 and 5		g, →	161,1			
Comp.	Weight, g	Catalyst		Finish			
MDI	58,0	1 drop Jeffcat T- 12		Thermal liberation difinitly disappears			
SR423D	24,2						
SR238	24,2						
2-HEA	33,8						
2-EH	21,0	2 drops Jeffcat T- 12		Thermal liberation difinitly disappears			
	0,0						
For preparing Cans 1 and 2 mixtures take				Cup 4 to 1 and 5 to 2		g, →	131,1
Content of the Component A in Cups 1 and 2:							
Bisomer PTE		in w. p.	in g.	in one Can			
Backbone		100	230	183	← CAN		
Bisomer PTE		0,5	1,15	0,9			
B8870		1	2,3	1,8	Backbone:	Content, %:	Assigned, %:
Parafine		6	13,8	11,0	TFUA	38	40
FCA 400		2	4,6	3,66	BFUA	19,665	20,7
Take for the Can from Cup 1 (Cup 2):				200,4	MFUA	37,335	39,3
Content of the Component B in the Ampoule:					SR-9020	5	
Ingredients		in w. p.		in g.			
Perkadox CH - 50L		2,5		4,6	← Ampoule		
		0		0,0			
TCPP		8		14,6			
Take from the mixture for the ampoule:				19,2			
The experiment is provided by:							
Approximate price of all used materials, EURO/kg:							4,95
Approximate price of the used chemicals for the Backbone only, EURO/kg:							3,60

		Tables for the Experiment:			Number of Experiment:		B6
TFUA:	Cup 3 and 4	172,6	g, →	158,7	plus	13,9	SR-9020
Comp.	Weight, g	Catalyst		Finish Criterion:			
MDI	55,2	1 drop Jeffcat T-12		Thermal liberation difinitly disappears			
SR604	27,4						
SR423D	24,1	1 drop Jeffcat T-12		Thermal liberation difinitly disappears			
SR238	24,1						
HPMA	21,0						
Glycerin	6,8	2 drops Jeffcat T-12		The viscosity steadily stops growing			
SR-9020	13,9						
For preparing Cans 1 and 2 mixtures take				Cup 3 to 1 and 4 to 2		g, →	142,6
MF/BFUA	Cup 5		g, →	204,8			
Comp.	Weight, g	Catalyst		Finish			
MDI	73,8	1 drop Jeffcat T- 12		Thermal liberation difinitly disappears			
SR423D	30,7						
SR238	30,7						
2-HEA	42,9						
2-EH	26,7	2 drops Jeffcat T- 12		Thermal liberation difinitly disappears			
	0,0						
For preparing Cans 1 and 2 mixtures take				Cups 1 and 2		g, →	87,4
Content of the Component A in Cups 1 and 2:							
Bisomer PTE		in w. p.	in g.	in one Can			
Backbone		100	230	183	← CAN		
Bisomer PTE		0,5	1,15	0,9			
B8870		1	2,3	1,8	Backbone:	Content, %:	Assigned, %:
Parafine		6	13,8	11,0	TFUA	57	60
FCA 400		2	4,6	3,66	BFUA	13,11	13,8
Take for the Can from Cup 1 (Cup 2):				200,4	MFUA	24,89	26,2
Content of the Component B in the Ampoule:					SR-9020	5	
Ingredients		in w. p.		in g.			
Perkadox CH - 50L		2,5		4,6	← Ampoule		
		0		0,0			
TCPP		8		14,6			
Take from the mixture for the ampoule:				19,2			
The experiment is provided by:							
Approximate price of all used materials, EURO/kg:							4,86
Approximate price of the used chemicals for the Backbone only, EURO/kg:							3,51

Figure 53 – Formulations B5 and B6



		Tables for the Experiment:			Number of Experiment:		B7
TFUA:	Cup 3	194,1	g, →	165,1	plus	29,0	SR-9020
Comp.	Weight, g	Catalyst		Finish Criterion:			
MDI	57,5	1 drop Jeffcat T-12		Thermal liberation difinitly disappears			
SR604	28,5						
SR423D	25,1	1 drop Jeffcat T-12		Thermal liberation difinitly disappears			
SR238	25,1						
HPMA	21,9						
Glycerin	7,1	2 drops Jeffcat T-12		The viscosity steadily stops growing			
SR-9020	29,0						
For preparing Cans 1 and 2 mixtures take				Cups 1 and 2		g, →	77,1
MF/BFUA	Cups 4 and 5		g, →	183,0			
Comp.	Weight, g	Catalyst		Finish			
MDI	65,9	1 drop Jeffcat T- 12		Thermal liberation difinitly disappears			
SR423D	27,4						
SR238	27,4						
2-HEA	38,3						
2-EH	23,9	2 drops Jeffcat T- 12		Thermal liberation difinitly disappears			
	0,0						
For preparing Cans 1 and 2 mixtures take				Cup 4 to 1 and 5 to 2		g, →	153,0
Content of the Component A in Cups 1 and 2:							
Bisomer PTE		in w. p.	in g.	in one Can			
Backbone		100	230	183	← CAN		
Bisomer PTE		0,5	1,15	0,9			
B8870		1	2,3	1,8	Backbone:	Content, %:	Assigned, %:
Parafine		6	13,8	11,0	TFUA	28,5	30
FCA 400		2	4,6	3,66	BFUA	22,895	24,1
Take for the Can from Cup 1 (Cup 2):				200,4	MFUA	43,605	45,9
Content of the Component B in the Ampoule:					SR-9020	5	
Ingredients		in w. p.		in g.			
Perkadox CH - 50L		2,5		4,6	← Ampoule		
		0		0,0			
TCPP		8		14,6			
Take from the mixture for the ampoule:				19,2			
The experiment is provided by:							
Approximate price of all used materials, EURO/kg:							4,94
Approximate price of the used chemicals for the Backbone only, EURO/kg:							3,59

		Tables for the Experiment:			Number of Experiment:		B8
TFUA:	Cup 3 and 4	172,6	g, →	158,7	plus	13,9	SR-9020
Comp.	Weight, g	Catalyst		Finish Criterion:			
MDI	55,2	1 drop Jeffcat T-12		Thermal liberation difinitly disappears			
SR604	27,4						
SR423D	24,1	1 drop Jeffcat T-12		Thermal liberation difinitly disappears			
SR238	24,1						
HPMA	21,0						
Glycerin	6,8	2 drops Jeffcat T-12		The viscosity steadily stops growing			
SR-9020	13,9						
For preparing Cans 1 and 2 mixtures take				Cup 3 to 1 and 4 to 2		g, →	142,6
MF/BFUA	Cup 5		g, →	204,8			
Comp.	Weight, g	Catalyst		Finish			
MDI	74,2	1 drop Jeffcat T- 12		Thermal liberation difinitly disappears			
SR423D	30,7						
SR238	30,7						
2-HEA	53,4						
2-EH	15,7	2 drops Jeffcat T- 12		Thermal liberation difinitly disappears			
	0,0						
For preparing Cans 1 and 2 mixtures take				Cups 1 and 2		g, →	87,4
Content of the Component A in Cups 1 and 2:							
Bisomer PTE		in w. p.	in g.	in one Can			
Backbone		100	230	183	← CAN		
Bisomer PTE		0,5	1,15	0,9			
B8870		1	2,3	1,8	Backbone:	Content, %:	Assigned, %:
Parafine		6	13,8	11,0	TFUA	57	60
FCA 400		2	4,6	3,66	BFUA	19	20
Take for the Can from Cup 1 (Cup 2):				200,4	MFUA	19	20
Content of the Component B in the Ampoule:					SR-9020	5	
Ingredients		in w. p.		in g.			
Perkadox CH - 50L		2,5		4,6	← Ampoule		
		0		0,0			
TCPP		8		14,6			
Take from the mixture for the ampoule:				19,2			
The experiment is provided by:							
Approximate price of all used materials, EURO/kg:							4,91
Approximate price of the used chemicals for the Backbone only, EURO/kg:							3,56

Figure 54 – Formulations B7 and B8

2.2.3 Density Analysis

Formulation	Mass of Specimen (g)	Length (cm)	Width (cm)	Mass of Water (g)	Density (g/l)
A1	14,8	11,5	17,6	298,8	44,68
A2	12,3	11,8	15,3	234,6	46,93
A3	11,3	11,2	17,2	245,6	40,42
A4	10,7	12,2	14,7	238,4	39,52
A4	10,4	12,5	15,4	234,2	38,56
A6	12,3	13,4	15,3	282,3	38,39
A7	11,1	12,6	15,2	257,4	37,82
A8	12,5	15,2	16,8	498,2	21,45
A9	11,7	13,2	17,7	398,6	25,19
A10	12,6	14,3	17,2	317,3	34,20
A11	10,3	12,5	17,7	254,6	34,29
A12	12,4	12,2	17,6	307,6	35,34
A13	13,5	10,3	16,1	296,2	41,55
A14	10,4	12,0	15,0	190,6	47,83
A15	14,2	11,8	16,8	187,2	68,27
B1	10,7	14,2	13,2	345,6	27,10
B2	7,6	9,5	9,5	412,4	16,85
B3	8,6	12,3	12,3	390,3	19,27
B4	10,4	9,8	10,3	390,4	24,77
B5	7,6	8,6	8,4	420,3	16,84
B6	11,5	9,4	10,2	397,2	27,19
B7	5,9	9,4	10,9	290,7	17,78
B8	12,3	10,3	11,8	335,6	34,03
B8A	17,2	9,4	8,9	334,6	49,53
B8B	13,9	8,3	10,2	312,2	42,52
B8C	12,9	9,5	11,2	280,3	43,26
B8D	11,2	10,3	12,3	256,2	40,15
B8E	13,4	10,1	9,6	356,5	35,59
B8F	14,1	9,8	10,4	342,4	39,00
B8G	13,2	10,2	10,6	298,2	41,62

Table 80 – Density Measurements

2.2.4 Physical tests

2.2.4.1 Adhesion and Compression tests

The obtained values presented in the compression test are a result of an average of the interpolation at 10 % strain. The ones of the adhesion test are a result at maximum strain ⁽¹⁾.

Formulation	Adhesion (kPa) Average max strain	Compression (kPa) Average at 10% strain
A1	15,1	32,6
A2	19,0	19,0
A3	20,5	39,2
A4	22.7	51,3
A5	20,9	47,1
A6	22,9	49,1
A7	23,9	55,9
A8	*	*
A9	*	*
A10	*	*
A11	*	*
A12	*	*
A13	27,2	70,2
A14	30,1	86,1
A15	61,9	45,6
B1	*	*
B2	*	*
B3	*	*
B4	*	*
B5	*	*
B6	*	*
B7	3,9	11,3
B8	6,7	8,8
B8A	9,2	12,4
B8B	10,8	17,6
B8C	8,4	16,7
B8D	8,6	13,0
B8E	7,2	11,5
B8F	11,0	26,1
B8G	32,2	36,8

Table 81 – Results of the Adhesion Test and Compression Test

2.2.4.1.1 *Adhesion Graphs*

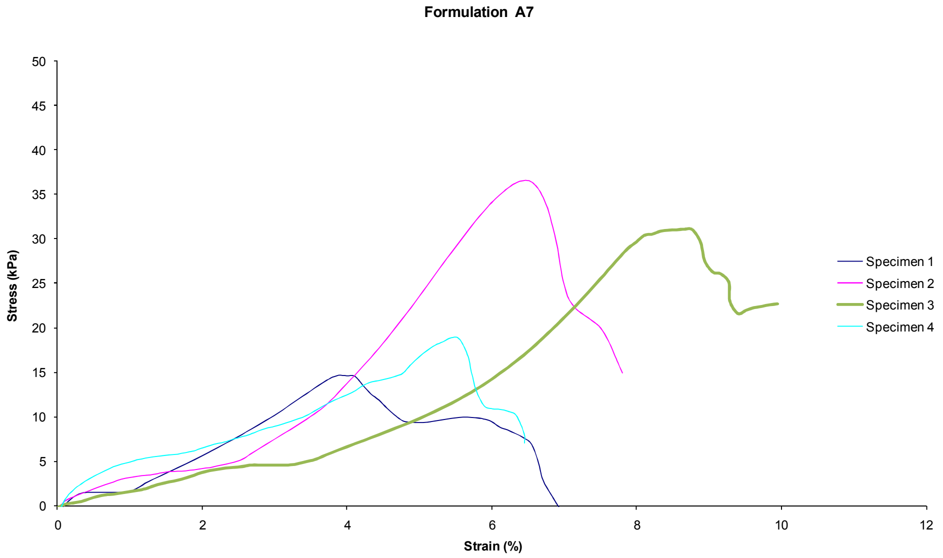


Figure 55 – Adhesion graph of 4 tests performed with Formulation A7 at T=23°C

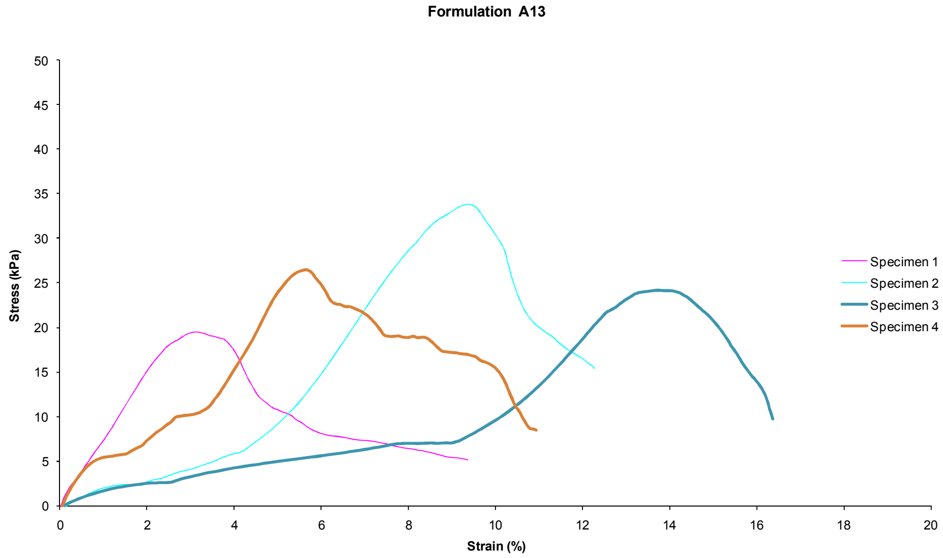


Figure 56 – Adhesion graph of 4 tests performed with Formulation A13 at T=23°C

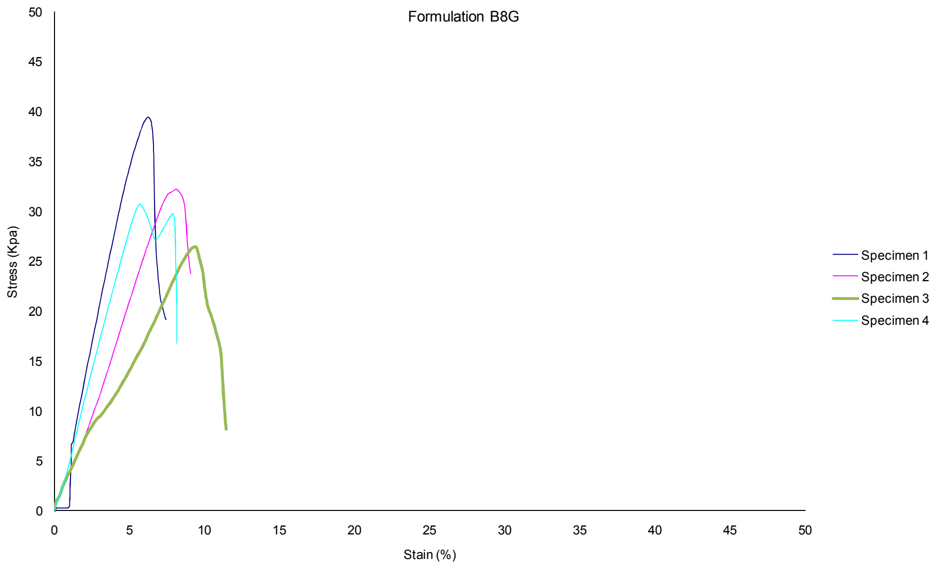


Figure 57 - Adhesion graph of 4 tests performed with Formulation B8G at T=23°C

2.2.4.1.2 *Compressions Graphs*

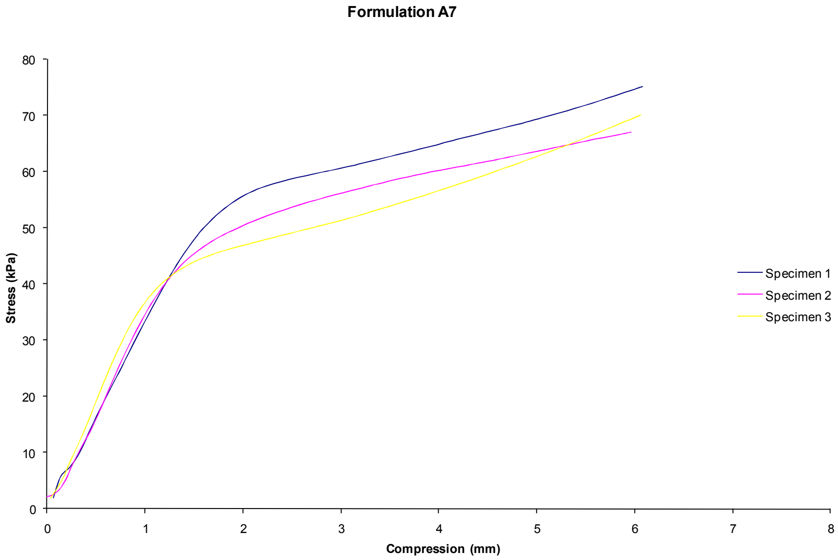


Figure 58 – Compression graph of 3 tests performed with Formulation A7 at T=23ºC

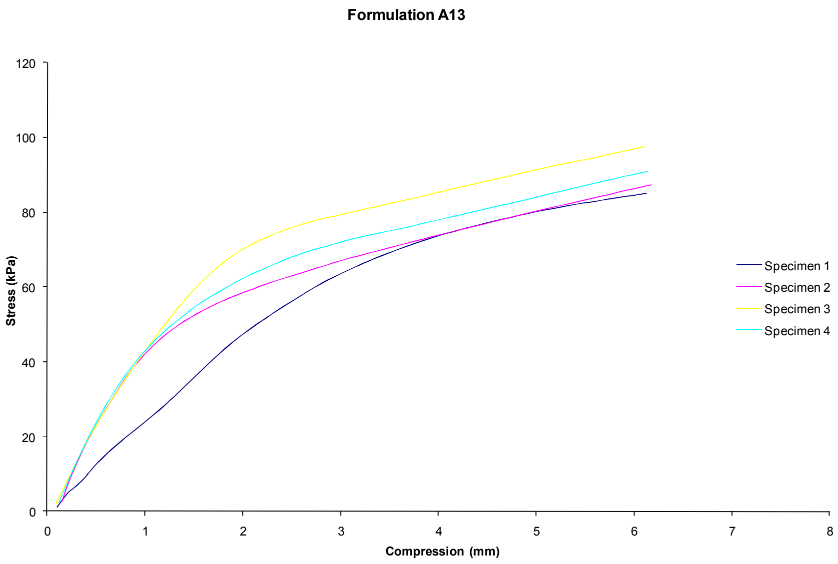


Figure 59 – Compression graph of 4 tests performed with Formulation A13 at T=23ºC

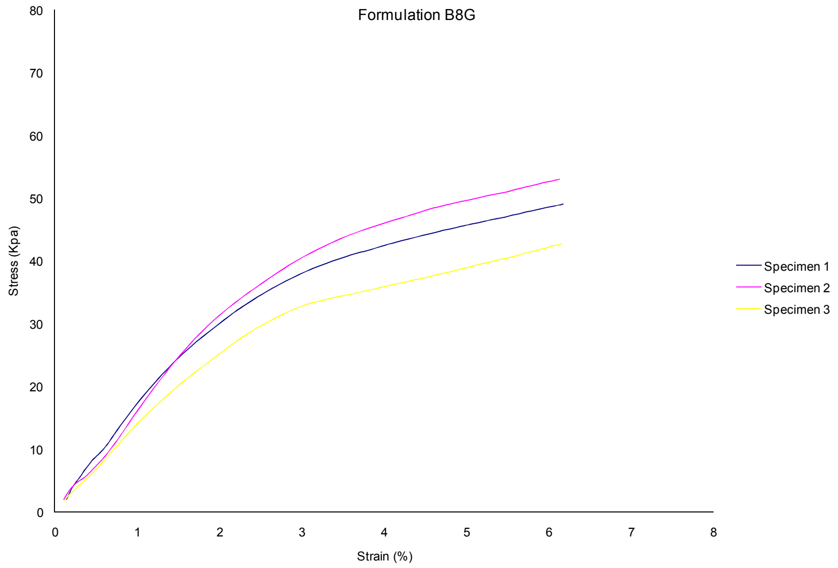


Figure 60 – Compression graph of 3 tests performed with Formulation B8G at T=23ºC

2.2.4.2 Shear Strength Test

As the results for the adhesion were quite satisfactory for the formulations A7, A13 and B8G, it was considered worthy to test these foams also on the shear strength test.

Formulation	Max Shear Strength Average (kPa)
A7	18,9
A13	27,9
B8G	20,5

Table 82 - Results of the Shear Strength Test

2.2.4.2.1 *Shear Strength Graphs*

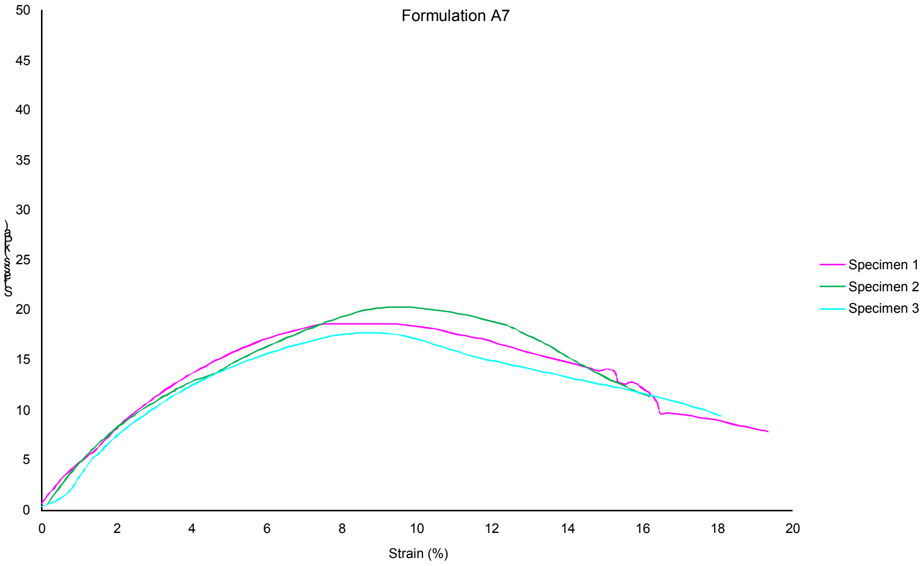


Figure 61 – Shear Strength graph of 3 tests performed with Formulation A7 at T=23°C

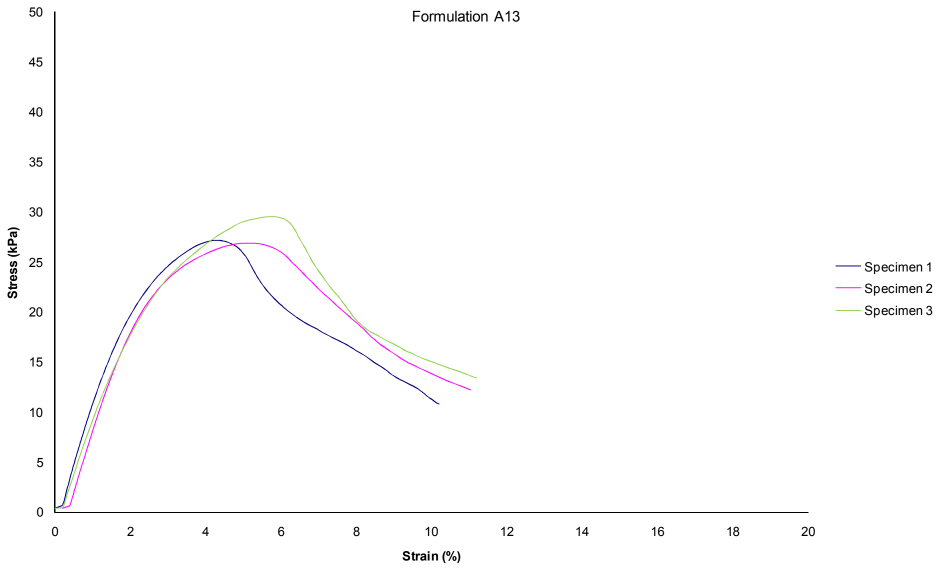


Figure 62 – Shear Strength graph of 3 tests performed with Formulation A13 at T=23°C

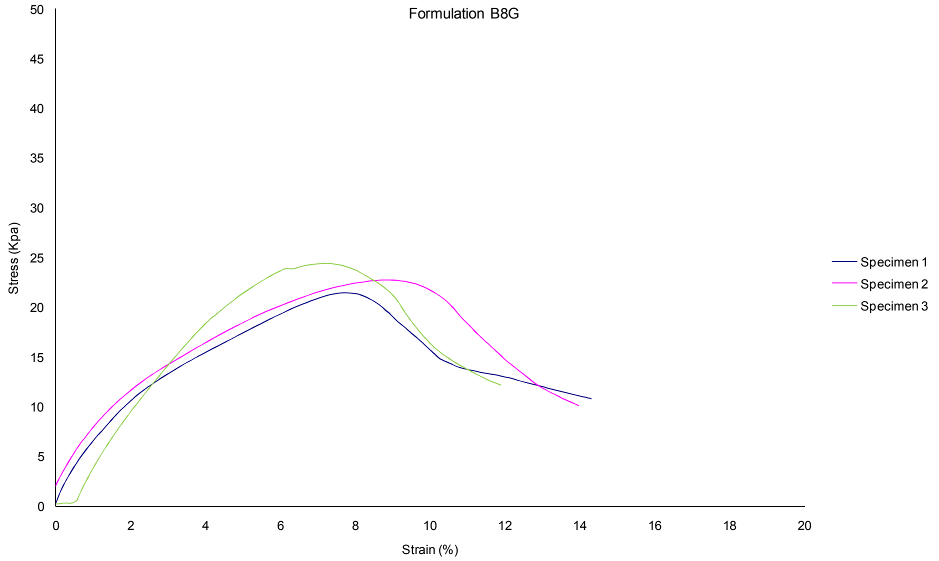


Figure 63 – Shear Strength graph of 3 tests performed with Formulation B8G at T=23°C

2.2.5 Alta Foam Monitor

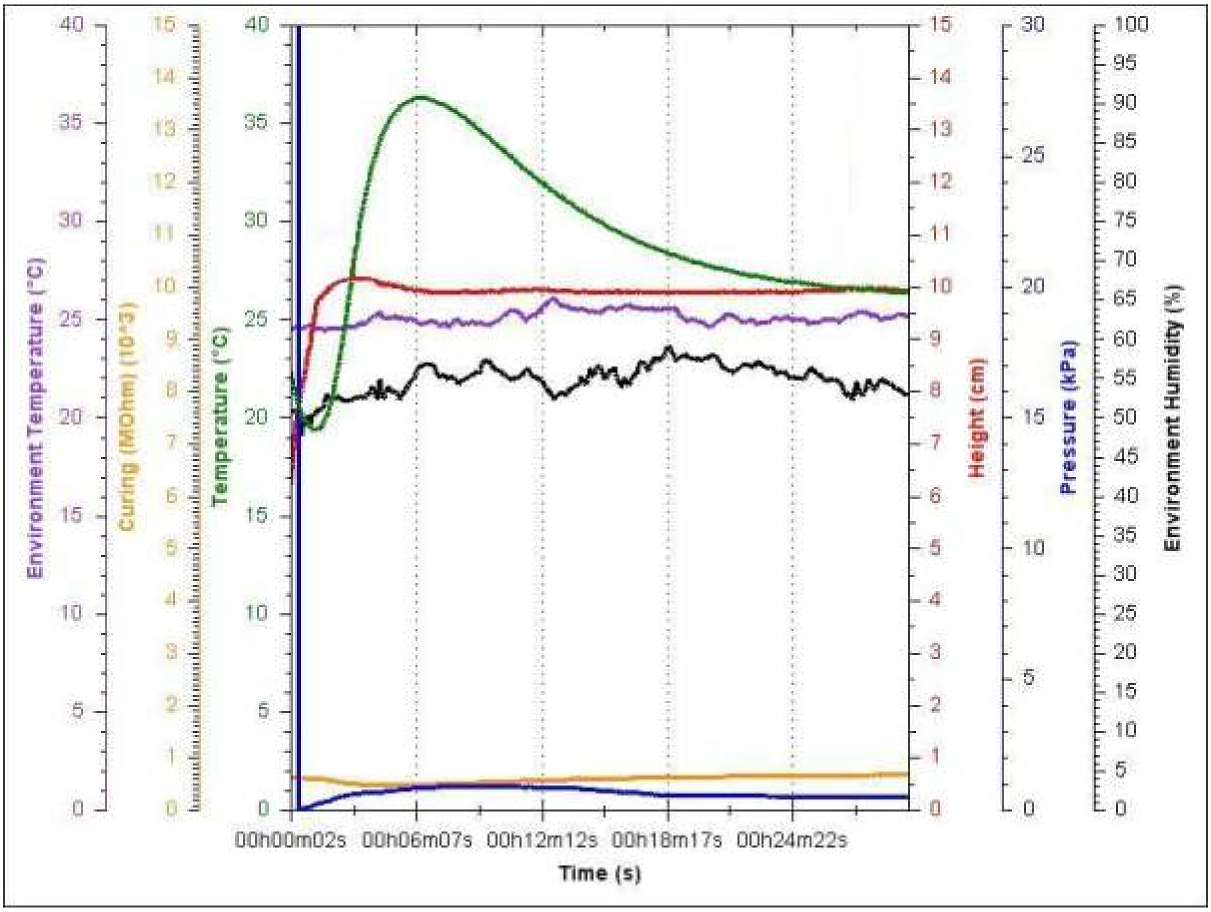


Figure 64 – Alta Foam Monitor Report

The graph shows the evolution of the different properties measured by the Alta Foam Monitor for the ECOFAST foam. As we can see after 7 minutes the foam is cured and no other properties changes after this minute. This graph also shows no post expansion or post shrinkage.

2.2.6 Economic Analysis

As referred since the beginning of this study, one of the main purposes was to evaluate an ecological foam system with a lower chemical cost. Therefore, in the following information it will be possible to observe the comparison between start and final formulations that we achieved as good results in this project.

The prices of the raw materials used have been taken from the formulation specifications sheet.

Products	Mass / g	Volume / ml	Price (€/kg)	Price/Can (€)
CN927B80	356,24	356,24	12	4,275
PPT1000TMA	41,49	41,49	3	0,124
B8870	19,36	19,36	6	0,116
TCPP	22,13	17,21	1,75	0,039
Paraffin	11,07	11,90	4	0,044
FCA 400	16,60	12,97	9	0,149
Perkadox CH-50L	2,80	8,28	5	0,014
Bisomer PTE	0,69	0,62	9	0,006
LPG	70,60	141,00	0,7	0,049
DME	17,60	26,40	1,2	0,021
Can	-	-	-	0,300
			Price per Can	**5,137**

Table 83 - Economic Analysis of the Formulation A7

Products	Mass / g	Volume / ml	Price (€/kg)	Price/Can (€)
PRO20652	356,24	356,24	15	5,343
PPT1000TMA	41,49	41,49	3	0,124
B8870	19,36	19,36	6	0,116
TCPP	22,13	17,21	1,75	0,039
Paraffin	11,07	11,90	4	0,044
FCA 400	16,60	12,97	9	0,149
Perkadox CH-50L	2,80	8,28	5	0,014
Bisomer PTE	0,69	0,62	9	0,006
LPG	70,60	141,00	0,7	0,049
DME	17,60	26,40	1,2	0,021
Can	-	-	-	0,300
			Price per Can	**6,205**

Table 84 - Economic Analysis of the Formulation A15

As seen on the figure 54 the Formula B8 the approximate price of all materials used is 4,91€.

3 Final Considerations

The good results obtained by the aliphatic (CN9278B80) and aromatic (PRO20652) versions of the Sartomer products were not sufficient to continue our study on their tuning-up due to their very high price. This price doesn't allow these foams to be commercialised.

At the moment we have some encouraging results on the base of the monomer structures:

1. Acrylic terminated urethane Prepolymers:

- Monofunctional urethane acrylate – Prepolymer of MDI, in which first ½ of NCO groups are connected with some alcohol with aliphatic chain – 2-Ethyl Hexanol (to neutralize this part of NCO groups with structure, preventing crystalline formation) and second ½ of NCO groups are connected with OH of some Hydroxy-acrylate, such as 2-hydroxyethyl acrylate;

- Bi-functional urethane Acrylate – Prepolymer of MDI, in which all NCO-groups of MDI reacts with mixture of 80% 2-Hydroxypropyl methacrylate (HPMA) and 20% SR604 (PPG300MMA, Polypropylene glycol M_w 300 monomethacrylate);

- Tri-functional urethane Acrylate - Prepolymer of MDI, in which first ½ of NCO groups are connected with mixture of HPMA and SR604, second ½ of NCO is connected with Glycerin.

The most important for stable results and performance is the preparation of all acrylic terminated Prepolymers to be composed by well-controllable reactions. The end of every reaction is indicated either by the end of the viscosity growth or by disappearing of the thermal liberation. By this reason it is very difficult to work with very long chain Polyols – reaction is going into diffusive area and it's very hard to determine its end.

2. Acrylic monomers, active diluents:

- 1,6 Hexanediol Diacrylate, 1,6 HDDA, SR238, very good solvent for the Urethane acrylates, very good gas acceptance, contributing to the toughness and with low shrinkage, bi-functional;

- Isobornyl methacrylate, IBM, IBMA, SR423D, smooth Polymerization, reduced reactivity, very good solvent for the Urethane acrylates, very good gas acceptance, gives hardness, mono-functional;

- Propoxylated Glyceryl triacrylate, SR-9020, giving stable cross-link, good solvent for the Urethane acrylates, contributing to the toughness.

4 References

1. **Schrijver, Aster De.** *Benchmarking and Classification of 1KPU Foams.* Deinze : s.n., 2001.

2. **Gong L., Kyriakides S., Jang WJ.** *Int J solid struct.* 2005.

3. **Liu C., Wei D., Zheng A., Li Y., Xiao H.** *J Appl Polym Sci.* 2006.

4. **Taki K., Tabata K., Kihara S., Ohshima M.** *Polym Eng Sci.* 2006.

5. **Nabar YU., Draybuck D., Narayan R.** *J Appl Polym Sci.* 2006.

6. **Kannanet.** *all. patent US 4.262.*

7. **Dominguez-Rosado E., Liggat JJ., Snape CE., Eling B., Pichtel.** *J. Polym degrad stabil.* 2002.

8. **G., Woods.** *The ICI polyurethane book.* New York : Wiley & Sons, 1985.

9. **Modesti M., Lorenzetti A., Besco S.** *Polymer Engineering and Science.* 2007.

10. **Jung HC., Ryu RC., KIM WN., Lee YB., Choe KH., Kim SB.** *J Appl Polym Sci.* 2001.

11. *Patent US 986.* **company, Pittsburgh plate glass.**

12. *Patent DE 3 616 100.* **al., Kinzebach et.**

13. *Patent US 4.314.036.* **al., Throne et.**

14. *Patent US 4.122.047.* **al., Stanislaw et.**

15. *Patent US 4.388.419.* **al, Murakami et.**

16. *Patent US 4.525.487.* **al, Ahnemiller et.**

17. *Patent US 4.304.876.* **al., Cozzi et.**

18. *Patent US 4.623.478.* **al., Pastorino et.**

19. *Patent US 3.823.099.* **al., Doyle et.**

20. *Patent EP 0 001 724.* **al., Michel et.**

21. *Patent EP 0 101 197.* **al., Ahnemiller et.**

22. *Patent EP 1 101 197.* **al., Harrison et.**

23. *Patent GB 2 031 900.* **al., Meisels et.**

24. *Patent US 712.* **Corporation, United Aircraft.**

25. **Kacperski M., Spychaj T.** *Polym Adv Technol.* 1999.

26. *Patent EP 0 001 724.* **al, Bloch et.**

27. *Patent US 1,216,158.* **al, Koerner et.**

28. *Patent US 1,253.* **Eib.**

X. 29. *Patent WO 93/24548.* **al., Brooks et.**

30. *WO 96/30438.* **al., Borden et.**

31. *Patent EP 0108 177.* **al., Ritter et.**

32. **Kim DJ., Kim SW., Kang HJ., Seo KH.** *J Appl Polym Sci.* 2001.

33. **Rahn, Sartomer &.** www.sartomer.com and www.rahn.ch. [Online]

34. **MO-01/1, IFT-Richtlinie.** *Baukörperanschluss von Fenstern.* 2001.

35. **Oliver Seely, Jr.** http://www.csudh.edu/oliver/satcoll/archmede.htm. [Online]

ANNEXES

5 Annexes

5.1 Some pictures of the trials performed

			
Picture 1 – Formulation A1	**Picture 2 – Formulation A2**	**Picture 3 – Formulation A3**	**Picture 4 – Formulation A4**
			
Picture 5 – Formulation A5	**Picture 6 – Formulation A6**	**Picture 7 – Formulation A7**	**Picture 8 – Formulation A8**
			
Picture 9 – Formulation A9	**Picture 10 – Formulation A10**	**Picture 11 – Formulation A11**	**Picture 12 – Formulation 12**

			
Picture 13 – Formulation A13	**Picture 14 – Formulation A14**	**Picture 15 – Formulation A15**	**Picture 16 – Formulation P2**
			
Picture 17 – Formulation P3	**Picture 18 – Formulation P4**	**Picture 19 – Formulation P5**	**Picture 20 – Formulation P8**
			
Picture 21 - Formulation P13	**Picture 22 – Formulation P15**	**Picture 23 – Formulation P16**	**Picture 24 – Formulation P18**
			
Picture 25 – Formulation P19	**Picture 26 – Formulation B1**	**Picture 27 – Formulation B2**	**Picture 28 – Formulation B3**
			
Picture 29 – Formulation B4	**Picture 30 – Formulation B5**	**Picture 31 – Formulation B6**	**Picture 32 – Formulation B7**

			
Picture 33 – Formulation B8	**Picture 34 – Formulation B8B**	**Picture 35 – Formulation B8D**	**Picture 36 – Formulation B8E**
			
Picture 37 – Formulation B8F	**Picture 38 – Formulation B8G**	**Picture 39 – Density Measurement by Archimedes's Principle**	**Picture 40 – Specimen for Mechanical Tests**
			
Picture 41 – Alta Foam Monitor			