

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

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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, CO₂, 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.

1 INTRODUCTION

The proposed project is on a new class of foam sealants based on "ACRYLATE TERMINATED URETHANE & POLYESTER OLIGOMERS" used for thermal & sound insulation.

The existing foamed sealants are one and two component PU foams (OCF = One Component Foams; TCF=Two component Foams) in aerosol cans and/or pressure vessels-

Those foams were developed by ICI Ltd in 1970 and are today worldwide used. They provide excellent mechanical properties and outstanding thermal insulation. Therefore they are widely used in the construction field for thermal and sound insulation and fixation of door frames and others.

These froths are cured by the reaction of the isocyanate terminated prepolymers with moisture.

All OCF's contain free monomers of crude MDI, which are critical with respect to toxicological and environment implications. Isocyanates are even suspected of causing cancer.

The European council is announcing new legislation regarding the labeling of the OCF cans. The labeling R40 (cancerogenic) and Xi is a must as from June 2009.

The typical property ranges can be seen in Table 1 .The minimum required physical properties should be independent from the ambient temperature, can temperature and from the age of the aerosol can or pressure vessel. The minimum requirements when a foam is kept and sprayed at 23°C with a relative humidity of 50 % (typical

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abbreviation 23°C-can temp/23°C-50% RH- ambient conditions) in case of filling and fixation foams are shown in Table 2.

PROPERTY	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 litres
Closed cells	60 – 70 %
Storage life	12 months when stored at 20 °C

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 foams at 23/23 °C –50% RH

In the OCF manufacturing process, at the first stage an aerosol can is filled of with a mixture of a polyol blend, isocyanate, different additives and physical blowing agent like Liquefied Petroleum Gases (LPG) and DME (Dimethylether). The pre-polymerization reaction occurs inside the can: the polyol is reacted with isocyanate which is abundantly in excess present.

At the second stage, while dispensing, the liquid prepolymer leaves the can and starts to expand to a low density froth by vaporization of the physical blowing agent.

Once exposed to the air, in the third stage, and in the presence of a chemical blowing agent (water), the reaction between water and the excess isocyanate will occur to form unstable carbamic acid which immediately decomposes into an amine and carbon dioxide, which will assure a second expansion of the foam.

It is also important to mention that the most common isocyanate that is used in the production of the PUF is the MDI, Methylene Diphenyl Diisocyanate. This compound, although the least hazardous of the isocyanate groups, is still toxic, harmful by

inhalation or ingestion, and also through skin contact. It is flammable and can also be explosive.

The use of environmentally friendly blowing agents as well as non-harmful catalysts has become an important and urgent issue in the synthesis of PU foam.

2 ECOFAST: Health – and Eco friendly fast curing foams

This route consists of using oligomers containing reactive end groups, with the same aim of getting good structural foams.

The choice of the oligomer is very critical; very often 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 ECOFAST system.

Examples of performance characteristics are:

- Reactivity
- Adhesion to various substrates
- Physical properties
- Applicable within a temperature range from -15°C up to +35°C

Often a combination of these properties is desired. In addition to this, cost is also a very important selection criteria.

Selection of the oligomers can be made on the basis of several criteria:

- The chemical family of the oligomer
- The functionality
- The molecular weight

The ECOFAST oligomers are having unsaturated backbones with reactive groups and different functionalities (monofunctional, bifunctional, trifunctional). General speaking the lower is the functionality, the lower the reactivity, the better the flexibility and the lower the viscosity. Functionality of two and three are good compromises for general purpose ECOFAST oligomers.

Monofunctional oligomers are used to improve adhesion to difficult substrates and to improve flexibility.

2.1 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.

Urethane Acrylate Oligomers

Mostly urethane acrylate (methacrylate) oligomers with different functionality, try to have the PU foams mechanical advantages. They bring specific favorable toughness to the foam, forming Urethane H - bond Net ($>N - H \dots O = C<$) 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.

Unsaturated Polyester Oligomers

Unsaturated polymers include polyesters like polyethylene terephthalate 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 extent 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 $\geq 2,5$, diluted by efficient Acrylate or Methacrylate (mono or bi-functional)

The curing of the unsaturated polyester resin and the acrylates oligomers is performed via a free radical mechanism in the presence of a monomer capable of crosslinking the polyester and acrylates..

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To initiate the reaction, a source of free radicals is needed. At low temperatures the reaction will be initiated by tertiary amines.

The radical chain polymerization route is nothing more than the crosslinkage of the double bonds of the UPEST resin, the URETHANE acrylates and the monomer.

In order to get the right foam properties a mixture of oligomers and monomers is needed. Acrylates are a family of polymers, which are a type of vinyl polymer. Acrylates are made from acrylates monomers, which are esters containing vinyl groups that are two carbon atoms, double-bonded to each other, directly attached to the carbonyl carbon.

Monomers are used as reactive diluents in formulations. For this, often low cost, multipurpose products are used. However, because sometimes quite high levels of monomers are used in the formulations, special to lower the viscosity, the influence of the monomer on the performance properties of the system can be significant.

In choosing the right monomers some parameters need to be taken into account such as:

- Functionality
- Type of chemical backbone
- Chemical structure (cyclic, branched or linear)
- Molecular weight

Beside the UPEST, Urethane and the acrylates backbone and monomers, other additives are needed to control the froth and curing process.

There are two different alternatives to initiate crosslinking reaction of UP resin with the monomer. They are the following:

- i) By radical initiation with organic peroxide or hydroperoxide.
- ii) Photochemically under ultra violet (UV) light using a photoinitiator.

The curing of polyester resin is performed via a free radical mechanism in the presence of a monomer capable of linking the polyester chains. The monomer also acts as a solvent in order to adjust the viscosity of the formulation and the performances of the final product.

To initiate the reaction a source of free radicals is needed. Organic peroxides are used as the source of free radicals. In the cold process, this reaction can be initiated by addition of metallic salts or amines, depending on the peroxide used.

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The selection of the peroxide will determine the kinetic of reaction and is also an important parameter for the "pot life" as the final part quality is linked to the peroxide used (aspect, curing efficiency and other).

This route consists of utilizing oligomers containing reactive end groups, with different functionalities or even mixtures of different oligomers with different functionalities.

Various additives are added to the oligomers such as:

Surfactants, Emulsifying agents, Rheology modifiers, Accelerator, Catalyst and Blowing agents

3 Experimental Work

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.

Figure 1 – Typical

AltaFAST 100 – A			AltaFAST 100 – B		
	Compounds	Parts/weight		Compounds	Parts/weight
Urethane Acrylate	UA 102	90	Initiator	FCA 601	4
Crosslinker	UA 103	10			
Silicone	B8870	1			
Catalyst	FCA 600	2			
Additive	FCA 400	2			
Gas	LPG	16			

ECOFast Formulation

3.1 Physical Testing and Density Measurements

It was performed different tests as compression, adhesion and shear strength. The overall density mould (ODM) was the method that was used for the measurement of density. This method is based on the Archimedes' Principle.

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Formulation	Density gr/l	Average Adhesion in kPa	Average Compression Strength at 10% in kPa	Average Shear Strength in kPa
A7	37,82	23,9	55,9	18,9
A15	68,27	61,9	45,6	27,9
B8G	41,62	32,2	36,8	20,5

Table 3 – Results of the Density, Adhesion Test, Compression Test and Shear Strength

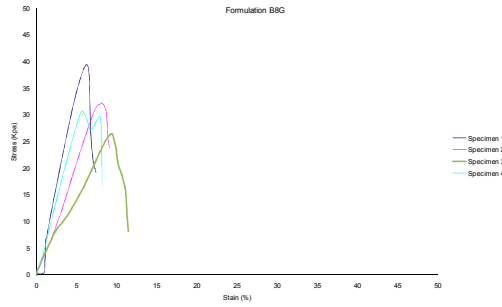


Figure 2 – Adhesion graph of 4 tests performed with Formulation B8G at T=23°C

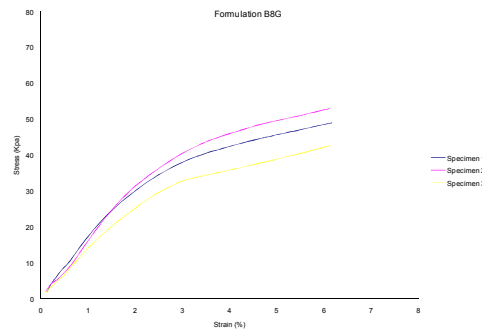


Figure 3 – Compression graph of 3 tests performed with Formulation B8G at T=23°C

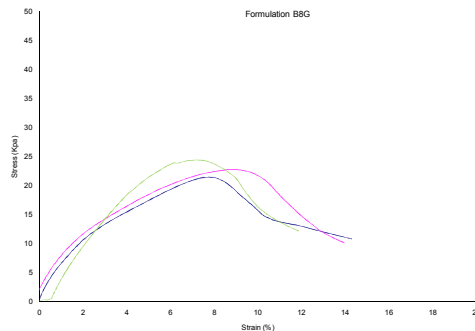


Figure 4 – Shear Strength graph of 3 tests performed with Formulation B8G at T=23°C

The best results obtained in this test were the ones performed using the foam containing paraffin in its composition.

For the ones with silicone the best results are obtained for the foams which lower amounts of it.

3.2 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.

Formulation	Price (€)
A7	5,137
A15	6,205
B8G	4,910

Table 4 – Price of the Final Formulations

4 Conclusions

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;

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- 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 $\frac{1}{2}$ of NCO groups are connected with mixture of HPMA and SR604, second $\frac{1}{2}$ 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.

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