The SafeRubber Project

June 2010 – May 2013

www.saferubber.eu

Scope

The **SafeRubber** collaborative project received funding under the European Seventh Framework Programme (FP7) for research for SME associations to develop:

'A Safer Alternative Replacement for Thiourea Accelerators in the Production Process of Chloroprene Rubber'

The project started in June 2010 and finishes at the end of May 2013

Polychloroprene (CR)

Often referred to as Neoprene® - DuPont trade name

- **Properties:**
  - Good weather resistance; sun, ozone, heat, water
  - Reasonable oil resistance
  - Self extinguishing
- **Common Uses:**
  - Wet suits
  - Weather seals
  - Oil seals
  - Gaskets
  - Adhesives
  - Cable insulation

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Project background
Competitive threat

The ***Safe Rubber*** Consortium represents associations and SMEs within the synthetic rubber processing sector, equating to over 6000 SMEs, employing over 360,000 people with a turnover of over €3.2 billion within Europe. The European SME synthetic rubber community is under pressure from three sources:

1. Market dominance by large enterprises, restricting SME suppliers/producers
2. Costs associated with EU health and safety regulations in the use of CRM classified accelerators
3. Increasing imports from low labour cost countries in the Far East (which do not have to meet European health and safety regulations)

Project background
Health risks of using ETU

- In chloroprene rubber, thiourea-based accelerators primarily ETU, remain in general the best cure system, giving a good balance between cure rate, scorch and physical properties
- With on-going concern over the potential carcinogenic and mutagenic risks of exposure to ETU, it would be highly desirable if an alternative could be found
- There is virtually no risk from ETU in the finished product under normal circumstances
- It is the dust and volatiles during processing which present the risk from ETU, in particular during the curing cycle. The dust problem can be eliminated by using a polymer bound dispersion. The volatiles prevent women of child bearing age from working with the compound
- It is anticipated that the use of ETU in the EU rubber industry could be jeopardized in the future by REACH legislation

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Project goal

The Project Consortium believes a solution has been developed that delivers:

- An IP protectable method for producing chloroprene rubber, with reduced costs associated with health and safety
- The elimination of a CMR substance which due to the costs of implementation of the REACH regulation could reduce the ability for the SME members to compete on cost with Far Eastern suppliers
- Reduced environmental impact through reduced use of heavy metal compounds (MgO and ZnO) and/or effluent hazards associated with the process – further reducing costs

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Project consortium partners (1)

- **Four rubber industry associations**
  - Assocomaplast - Italian plastics & rubber machinery assoc. *Project coordinator*
  - ETRMA, European Tyre and Rubber Manufacturers' Association
  - Federplast.be, Belgian plastics & rubber industry association
  - BRPPA, British Rubber and Polyurethane Products Association
- **Four SME rubber companies**
  - Clwyd Compounders Limited, rubber compounder, UK
  - Mixer SPA, rubber compounder, Italy
  - MGN Transformaciones Del Caucho SA, rubber moulder, Spain
  - Robinson Brothers Ltd , rubber chemicals manufacturer, UK

Project consortium partners (2)

- **Four research institutes**
  - MatRI – UK Materials Technology Research Institute (Part of Pera Technology) *Project management*
  - Grand Synthesis, Latvia
  - UNIMIB, University of Milano, Italy
  - Norner Innovation, Norway

Project consortium partners (3)

Chloroprene rubber

Better understanding of the curing system (1)

1. The initial phase of work in the project was to develop a more comprehensive understanding of the mechanism of the existing accelerator system, based upon ETU, MgO and ZnO
2. Conducting a robust mechanistic study of the curing reaction using low molecular weight chloroprene oligomers to establish a model of the mechanism of the accelerator system
3. Confirmation of the mechanism by reacting existing accelerator with gumstock resin at normal molecular weights, and fully characterising the products formed
4. Computation analysis to probe the mechanisms already laid out in literature and to give additional insight into the curing mechanism. Quantum mechanical calculations were performed on molecules and species of interest in several reaction mechanisms relevant to the cross-linking of chloroprene rubber

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Chloroprene rubber

Better understanding of the curing system (2)

- Unlike rubbers such as NR, SBR, NBR and EPDM, the curing or cross-linking of chloroprene compounds is undertaken without using sulphur. Most conventionally used accelerators such as dithiocarbamates, thiurams, mercaptobenzothiazoles and sulphanides are not as effective, or have different effects in chloroprene rubber
- In general, the best properties are obtained by a cure system containing a combination of metal oxides (4phr of MgO and 5phr of ZnO) with 1phr ETU.

Chloroprene rubber

Better understanding of the curing system (3)

- The exact mechanism of chloroprene curing has never been fully understood, due, in part, to the fundamental lack of analytical techniques available during development stages (pre 1960s). Previous understanding thought that:
  - ZnO reacts with halogen groups to produce an active intermediate, which then reacts further to produce carbon–carbon cross-links
  - $ZnCl_2$ is liberated as a by-product and it serves as an auto catalyst. MgO scavenges excess $ZnCl_2$ to control the cure rate and minimise premature cross-linking. $ZnCl_2$ can also accelerate the dehydrochlorination of chloroprene, resulting in a deterioration of the rubber
  - It is therefore, essential to develop a system that produces no $ZnCl_2$ or one that prevents the $ZnCl_2$ from reacting

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Chloroprene rubber

Better understanding of the curing system (4)

- Cross-linking by ETU is reported to proceed via bisalkylation of ETU by the polymer chain at the active chlorine position
- These mechanisms imply that cross-linking with both ZnO and ETU are linear in nature; it does not appear to give a 3-dimensional network structure, which is required for good tensile and other properties of the cross-linked rubber
- Therefore, in order to explain the excellent cross-linked rubber properties of CR, other mechanisms must be involved

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Chloroprene rubber

Study of the accelerator mechanism (1)

- Curing experiments completed on oligomers and chloroprene polymers with a range of accelerators
- All of the main rubber accelerator groups were represented whether or not they are generally used in CR compounds:
  - Sulphenamides: CBS
  - Thioureas: ETU, LATU
  - Thiazols: MBTS
  - Thiurams: TMTD
  - Dithiocarbamates: ZDBC, ZDEC
  - Others: EU, HPCA, HEXA, MTT, sulphur, zinc chloride, piperazine

Chloroprene rubber
Study on the accelerator mechanism (2)

- Previous literature studies and experimental observations state that rather than one curing mechanism taking place during the crosslinking of chloroprene, two, three or possibly more reactions are taking place at various rates:
  - ETU can cross link chloroprene alone in the absence of metal salts but it is unlikely to proceed *via* the published mechanism
  - ZnO can also cross link chloroprene alone and clearly proceeds by a different mechanism to that of ETU
  - ZnO and ETU react differently again
- This combination of mechanisms makes analysis of data from experimental studies extremely complex

Chloroprene rubber

Study on the accelerator mechanism (3)

Main observations:

- ETU does not act catalytically and is consumed in the cross linking process
- No strong evidence for the formation of ethylene urea during the cross linking process
- Thione-type compounds are important for initiation and the ability to stabilize the forming positive charge through electron resonance is also important
- As ETU appears to react via sulphur and not nitrogen, it should be possible to substitute nitrogen for other heteroatoms
- As TMTD is also active as an accelerator, it appears that the molecule does not have to be cyclic

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Study on the accelerator mechanism (4)

- The data obtained in this study on 14 different industrially available accelerators has been used as an input for Quantative Structure Activity Relationship (QSAR) modeling to define possible alternative accelerator molecules
- Experiments were undertaken to obtain data for four rheological properties:
  - **Optimum cure time**
  - **Scorch time**
  - **Minimum and maximum torque**
- and four mechanical properties
  - **Elongation at break**
  - **Hardness**
  - **Modulus at 100%**
  - **Tensile strength**

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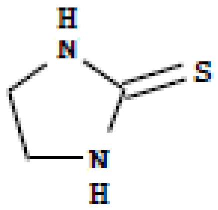
ETU accelerator system
Toxicological assessment (1)

ETU basic data



CAS-no.	96-45-7
EC-no.	202-506-9
Index-no.	613-039-00-9
T_m (°C)	197-201
M_w (g/mol)	102.16

Name: Imidazolidine-2-thione (EINECS)

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ETU accelerator system
Toxicological assessment (2)

ETU has been classified as

- Reproductive Toxicant Category 1B
- Hazard statement H360D – “may damage the unborn child”

- Long term exposure to ETU has shown it to be carcinogenic and teratogenic (causing malformation in offspring) in laboratory animals
- Epidemiological studies on workers exposed to dithiocarbamates or ETU did not show any increase in the incidence of thyroid tumours. However, only a relatively small number of workers was involved.
- ETU is considered as being of low concern as potential endocrine disrupter

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REACH

Potential consequences for ETU (1)

- ETU is classified as CMR (**Carcinogenic, Mutagenic or Toxic to Reproduction**) and is therefore a substance that fulfils the criteria for being identified as Substance of Very High Concern (SVHC) and therefore as a future candidate to be included in Annex XIV of REACH authorisation

REACH

Potential consequences for ETU (2)

- ETU has been identified as a Substance of Very High Concern (SVHC) and thereby added to the Candidate List, however REACH experience so far shows that it takes a long time for a substance to enter in Annex XIV (3-5 years) after being identified as a SVHC

Selection of candidate substitute molecules by QSAR methodology (1)

- QSAR methodology is the process by which a chemical structure is quantitatively correlated with a well-defined process, such as biological activity or chemical reactivity. Drug discovery often involves the use of QSAR to identify chemical structures that possess the specified levels of activity without the levels of toxicity
- Literature reviews revealed that QSAR has not been used in the field of rubbers yet. This project can be considered as the first attempt to establish quantitative relationships between structural features of CR accelerators and their properties. These relationships can be useful to estimate properties of untested accelerators in order to select the best accelerator candidates and assist with the mechanistic understanding

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Selection of candidate substitute molecules by QSAR methodology (2)

- An extended library consisting of 192 potential accelerators was compiled on the basis of two procedures:
  1. Library design on nine chemical scaffolds: 69 molecules defined
  2. 115 molecules added based on structural similarity to safe molecules obtained by QSAR analysis with seven reference accelerators molecules
- Integrated with twenty additional molecules proposed by the expert group within the Consortium

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Selection of candidate substitute molecules by QSAR methodology (3)

- The following indicators were defined to be relevant to the selection of replacement accelerators:
    1. Safety/toxicity
    2. Cross linking and mechanical performance
    3. Potential economic cost of synthesis
    4. Potential feasibility of synthetic route

Selection of candidate substitute molecules by QSAR methodology (4)

- A number of different QSAR tools were selected which were designed to meet REACH requirements and to get a prediction of carcinogenicity, mutagenicity, developmental toxicity, skin sensitization, bioaccumulation and biodegradability:
  - OECD
  - QSAR Toolbox
  - CAESAR
  - ToxTree
  - Lazar

Selection of candidate substitute molecules by QSAR methodology (5)

- Potential accelerators were ranked by mathematical and statistical approaches related to Multi Criteria Decision Making (MCDM)
- In conclusion, 15 potential accelerator molecules were selected to be considered for further experimental evaluations. These molecules are identified as SRMs (Safe Rubber Molecules)
- 12 were classified as being safer than ETU by using QSAR tools

Identification of synthesis routes to potential accelerator molecules

- Synthesis routes were defined for 12 possible accelerator molecules
- Synthesis of each molecule was carried out on a 20g scale for further investigations of the CR cross-linking process
- Characterization of the chosen molecules was done by NMR spectroscopy to confirm successful molecule preparation and purity

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Cure efficiency assessment of potential accelerator molecules

- A generic rubber formulation was produced as a Masterbatch for testing the newly synthesized molecules to assess their suitability as a potential ETU replacement
- Lab-scale rubber compounding trials were undertaken

Basic Masterbatch	
Ingredient	**Parts per 100 rubber (phr)**
Chloroprene rubber: Denka S40V, (Equivalent to DuPont Neoprene WRT)	**100.00**
Stearic Acid	**1.00**
Magnesium Oxide (MgO)	**4.00**
Zinc Oxide (ZnO)	**5.00**
Total	

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Cure efficiency assessment of potential accelerator molecules

- An indication of cure efficiency was obtained by deducting the figure for the minimum rheometer torque from the maximum torque, a low figure showing little cure and a high figure a good state of cure
- From examining the results of the trials and comparing them to well-known parameters such as those of ETU, it can be stated that a cure efficiency of over 78 shows a good state of cure
- Those which cured were moulded and their physical properties assessed : hardness, tensile strength, modulus at 100% and 300% (if applicable), and elongation at break

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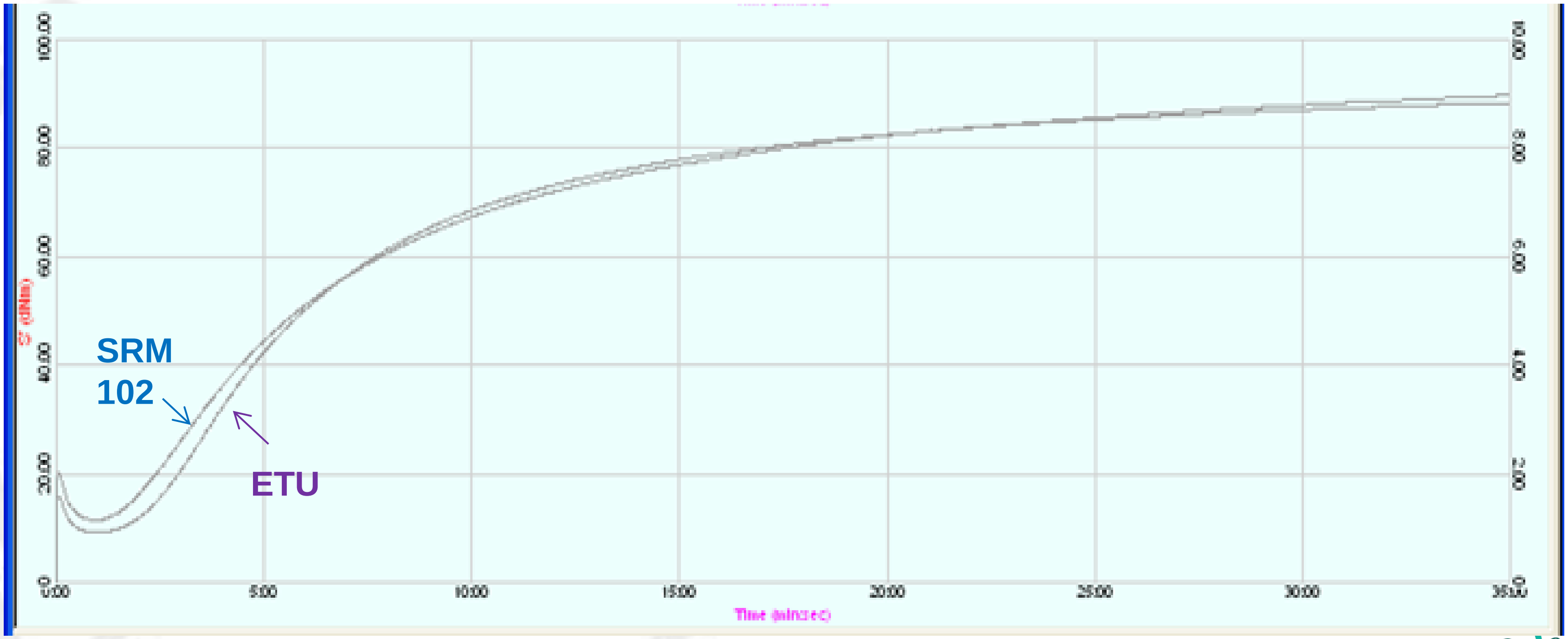
Cure efficiency assessment of potential accelerator molecules

Two molecules SRM102 and SRM104 showed cure characteristics comparable to ETU and were chosen for scale up trials. A comparison of SRM102 with ETU is shown below:



Synthesis of the selected accelerator molecules

- The synthesis of the two candidate molecules was complicated and accompanied by the formation of several by-products
- A new, reproducible procedure for the preparation of the target products on a 1 kg scale as one batch syntheses was developed
- The bulk synthesis compounds were analyzed and the results compared to the compounds synthesized on a small scale (20 g). Analysis showed that the compounds were chemically identical
- Accelerator **SRM102** was obtained in a 1kg batch trial with a purity of 97.5%
- Accelerator **SRM104** was obtained in a 1kg batch trial with a purity of 99.1%

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Final selection of the accelerator molecule

- Both molecules SRM102 and SRM104 have been classified as potentially *not* mutagenic, not carcinogen and *not* skin sensitizers
- SRM 102 was chosen for scaling up as it gave the best physical properties

Industrial validation trials

Chemical synthesis

- The synthetic route developed by GSL for SRM102 was validated by Robinson Brothers Ltd at both laboratory and then kilo lab scale to determine the robustness of the process and to ascertain that the process meets all health and safety parameters for scale up in the pilot plant
- The quality of the accelerator molecule manufactured by Robinson Brothers Ltd was verified by comparison with a sample from GSL
- A bulk quantity of SRM102 was manufactured by Robinson Brothers Ltd and quantities have been sent to Mixer, MGN and Clwyd Compounders for use in industrial validation trials

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Industrial validation trials
Rubber products manufacturing

- Guidance notes for industrial validation trials were produced and sent to all partners
- The three rubber producing endusers Mixer, MGN and Clwyd Compounders produced rubber compounds to their own formulations suitable for the following applications:
  - **Moulding – compression and injection**
  - **Extrusion – continuous and autoclave cure**
  - **Cable manufacture**
- Industrial trials have also been performed by two non-consortium companies who have provided valuable assistance:
  - **Nufox Rubber**
  - **BD Technical Polymer**

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New accelerator molecule
Evaluation of the performance characteristics

- All the experiments performed by the extrusion partners show that SRM102 could be an effective replacement of ETU in chloroprene based compounds. Crosslinking density, hardness, scorch safety, mechanical properties and more important, ageing resistance is very close to what is obtained using ETU

- Both general purpose and high-quality SRM102 compounds show good basic properties when compared with ETU containing compounds

- Properties can be optimised further by the addition of secondary accelerators giving a boosting or retarding effect

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New accelerator molecule

Evaluation of the REACH requirements (1)

- REACH Regulation gives different requirements for phase-in (existing) substances and non phase-in substances
- SRM102 the new SafeRubber accelerator will most likely be a non phase-in substance
- Non phase-in substances that are manufactured (or imported) >1000kg pa will have to be registered by the company before the start of its activities involving these substances

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New accelerator molecule

Evaluation of the REACH requirements (2)

In cases where the substance has not been previously registered, the following procedures need to be followed:

1) Carry out all tests required to satisfy registration requirements, alone or with other possible applicants
2) Testing on vertebrate animals must be avoided by making use of available data, read-across or results validated by QSAR models, if this is sufficient for the purpose of registration

New accelerator molecule

Evaluation of the REACH requirements (3)

- SRM 102 is a salt and this gives problems with some QSAR predictions, e.g. of physicochemical properties. This means that most of the physicochemical properties need to be determined by practical measurements

New accelerator molecule
Environmental assessment

- The environmental assessment of the new molecule will be completed by the end of the project in May 2013
- This assessment will include LCA (Life Cycle Analysis) and the potential of reducing or replacing ZnO in the compound
- Leaching trials are being carried out on SRM102 compounds

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New accelerator molecule
Commercial feasibility evaluation

- A commercial feasibility study was undertaken to ensure that the development of a replacement accelerator molecule was commercially viable (i.e. cost competitive to the use of state-of-the-art materials)
- The criterion used was that the manufacturing cost of a final rubber compound should be no more than 105% of the equivalent compound using ETU
- Robinson Brothers Limited have completed a preliminary calculation of the manufacturing cost of SRM 102 and inputted this into the model developed by MatRI. This model is complicated as it has been developed for different markets. It has shown that at the predicted % addition of SRM102, the increase in compound cost will be <5% i.e. it meets the target
- The relative cost of accelerator SRM102 should not act as a brake on its commercial viability

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General conclusions

- A molecule safer than ETU has been produced for cross linking chloroprene rubber

- Testing for REACH evaluation is currently being carried out

- Industrial trials have shown that SRM102 is an effective replacement for ETU in both general purpose and high-quality chloroprene based compounds

- SRM102 compounds show good basic properties

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