



The Safe Rubber consortium comprises 12 partners ((SME Associations (Assoc, FED, European Tyre and Rubber Manufacturers' Association, British Rubber and Polyurethane Products Association Limited), SME's (Robinson Brothers Ltd, Clwyd Compounders, MGN Transformaciones del Caucho, Mixer S.p.A, Promaplast) and RTD providers (Grand Synthesis Latvia SIA, University of Milano-Bicocca, The UK Materials Technology Research Institute Ltd)) from 5 countries and represent the SME communities within the synthetic rubber manufacturing and processing sector, equating to over 6000 SMEs, employing over 360,000 people and 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 carcinogenic accelerators
3. Increasing imports from low labour cost countries in the Far East (who do not have to meet EU health and safety regulations)

Generally, thiourea-based accelerators are used in the vulcanisation of polychloroprene rubber, primarily ethylene thiourea (ETU), as it produces the highest performance rubber cure system. However, ETU has been classified as a CMR substance (Carcinogenic/Mutagenic/Toxic for Reproduction) under the REACH Regulation. This means that ETU most likely will enter the Candidate List severely limiting its use and will in turn have a massively negative impact on the SME members, who are already under threat.

UNDERSTANDING THE CURING MECHANISM

In order to design a suitable ETU replacement in the SafeRubber project, the precise mode of action of ETU must be understood. To begin to understand this, a review of published work was undertaken to compare the already-suggested mechanisms and to further guide subsequent experimental work. The review highlighted three published curing mechanisms to be further investigated. The overall conclusion from this preliminary analysis was that the suggested mechanisms for the curing of chloroprene in the literature were possible but contained a number of unlikely transition states and intermediates.

In order to design better curing agents for chloroprene rubber, studies of the curing mechanism using advanced analytical techniques and computational methods continued. Using both chloroprene oligomers and gumstocks, Fourier Transform infra-red (FTIR) spectroscopy and gas chromatography-mass spectrometry (GC-MS) were employed to probe structural changes in the compounds to try to identify what is happening during crosslinking.

FTIR spectroscopy was used to monitor the disappearance of the band at 925 cm⁻¹ (attributed to the C=C group in the 1,2-isomer) during crosslinking without additives and with ethylene thiourea (ETU), ZnO, and both ETU and ZnO together. It was discovered that there was a 90% reduction of the 1,2-isomer within one minute and the remainder disappears

within 10 minutes. This is slower than with ZnO alone and suggests that there is a strong interaction (or complexation) between ZnO and ETU, which competes with the reaction of ZnO with the 1,2-isomer.

The published mechanism indicated that ETU reacts first with polychloroprene, before ZnO. However, we have strong evidence against this, as our kinetic study shows that ZnO reacts significantly faster with polychloroprene. Our computational analysis work also disagrees with the published mechanism and supports our own proposed mechanism.

The above observations gave further confirmation of our understanding of the mechanisms occurring and allowed us to design new, safer accelerators that have been shown to be highly active for the curing of chloroprene.

During the final period of the project, work has continued to understand the mechanism of curing of chloroprene rubber. It has been found that, as expected, the mechanism of curing changes depending on the chemical used as the crosslinking agent. However, it has also been noted that proposed mechanisms of curing do not act independently and the FTIR data and tensile testing results suggest multiple cross-linking reactions take place, depending on the curing agent used; when thioureas are used, bisalkylation dominates cross-linking; when thioureas with zinc oxide are used, sulphur cross-linking dominates; when bases are used, cationic crosslinking dominates. Our results lead us to the conclusion therefore that the mode of action of ETU cannot simply be described as one mechanism, but rather is a combination of multiple crosslinking reactions which change depending on the reaction conditions employed.

MOLECULAR DESIGN OF REPLACEMENT ACCELERATOR AND LAB SCALE TRIALS

For the QSAR (quantitative structure activity relationship) modelling of the replacement accelerator molecules a thorough literature review was been carried out to understand how and the extent to which QSAR could be used to estimate accelerator properties. It concluded that so far the use of QSAR to this end has not been exploited. A comprehensive bibliographic collection, which currently comprises 105 scientific papers related to different aspects of the world of rubbers, was generated. However a lot of the data generated was classed as not reliable enough to develop QSAR model on chloroprene rubbers, due to noise of inter-laboratory variance. As a consequence practical trials were carried out to collect the required raw data. 16 accelerators were mixed with a Masterbatch of gumstock and MgO/ZnO (current standard mix ratio) and optimised using rheometry allowing the following data to be generated for the QSAR modelling:

T min (minimum torque of uncured compound)

T50 (torque at 50% cure)

T final (torque at end of test [35 minutes])

Maximum torque during cure

Cure graphs

Tensile strength of vulcanisate

Modulus at 100% elongation

Modulus at 300% elongation

Elongation at break

Hardness

A statistical analysis of the mechanical and rheological properties of different compounds was undertaken by means of multivariate statistical tools (Principal Component Analysis) in order to understand the role played by different factors (type of accelerator, type of

formulation, type of filler, type of rubber) in defining the rubber properties. A pattern mainly related to the bibliographic source was discovered.

Existing QSAR models that relate chemical structures of substances to toxicological properties were evaluated and their efficiency was compared. Activities were initially focussed on a thorough review of documents on toxicological end-points relevant to REACH, along with QSAR scientific papers. A screening of existing QSAR applications (i.e., CAESAR, TOXTREE, LAZAR, EPISUITE, QSAR TOOLBOX, SPARC, PBT PROFILER, VCCLAB, ONCOLOGIC) was carried out and the toxicological end-points provided by each were evaluated, the reliability of the predicted toxicological values, as well as their applicability domain, focussing on persistence, bioaccumulation, toxicity, toxicological, ecotoxicological and physicochemical properties.

A number of QSAR (Quantitative Structure Activity Relationship) models were selected to predict toxicological properties of accelerator candidates. QSAR models relate measurements on a set of "predictor" variables to the behaviour of the response variable. In QSAR modelling, the predictors consist of properties of chemicals; the QSAR response-variable is the biological activity of the chemicals. The following properties were taken into consideration: bioaccumulation, biodegradability, carcinogenicity, skin sensitization, mutagenicity, aquatic acute toxicity, acute oral toxicity and developmental toxicity. Toxicological profiles of specific molecules were carried out including accelerators HEXA, HVA, MTT and the alternative ETU replacement (SD75) offering from MLPC.

A statistical QSAR approach to predict curing properties of accelerators was undertaken to relate the structural features of accelerators (encoded by molecular descriptors) to their curing properties in order to predict properties of untested accelerators and therefore provide information for the selection of the best accelerator candidates. The properties to be modelled were defined; these were TS2 (scorch time), T90 (optimum cure time), minimum torque, maximum torque, the binary variable cured/not cured, tensile strength, modulus 100%, modulus 300%, elongation at break and hardness and a large set of 1650 molecular descriptors expected to be related to the curing properties was calculated. In order to get reliable QSAR models for curing properties of accelerators, experimental data for a set of commercial accelerators were provided by MaTRI.

In order to produce the list of accelerator molecules to take forward it was necessary to define the chemical space that included potential accelerators and all the information needed to find a replacement accelerator molecule with similar performance to thiourea based accelerators, while avoiding their negative toxicological effects towards human health and environment. Initially, potential accelerator candidates were selected and included in an extended library on the basis of the following procedures: a) library design on chemical scaffolds suggested by the SafeRubber consortium and b) screening of "safe" molecules in toxicological databases through structural similarity analysis to existing accelerators. The mode of action of the accelerator system is still not fully understood (see above); however, knowledge and experience within the SafeRubber consortium led to the proposal of an additional number of molecular structures with curing potential.

Toxicological scores, mechanical, rheological, physicochemical properties and the indicators of economic cost and feasibility of a synthetic route were evaluated for each molecule in analysis and finally combined to define a global accelerator score by means of Multicriteria Decision Making strategies. This global accelerator score accounted for all the relevant information of each molecule and allowed the molecules to be ranked from the most to the least preferable ones. All of the aforementioned indicators were evaluated for each molecule included in the extended library of potential accelerator candidates. This work was undertaken computationally by applying QSAR tools or through literature review in order to

reduce time and costs of analysis and avoid animal testing. Toxicological profiles based on QSAR predictions were also evaluated for all of the molecules proposed on the basis of experts' knowledge about the vulcanisation process in order to ensure toxicological safety of the final selected accelerators.

A final list of 15 molecules/accelerators was selected considering both the molecules selected from the extended library and the molecules proposed by experts within the SafeRubber consortium. These molecules were labelled as SRM (SafeRubber Molecules) and were submitted to a deeper toxicological evaluation based on both QSAR models and a thorough search for experimental data by means of the available toxicological databases. The SRM molecules were divided in three classes on the basis of their toxicological profiles in order to produce a priority list for synthesis. The first class (A) included 7 molecules predicted as potential non-mutagen, non-carcinogen and non-skin sensitizer. The second class (B) included 5 molecules predicted as potential non-mutagen, non-carcinogen and skin sensitizer. The last class (C) included the remaining molecules (3) which could not be included in Class A or Class B. Finally, the toxicological profile of ETU was compared with those of the 15 SRM accelerators. All 15 selected accelerators can be considered potentially safer than ETU, this being classed as carcinogen and mutagen on the basis of experimental results and classed toxic to reproduction in the CLP regulation.

It was decided to initially only synthesise molecules from list A and B and these were synthesised on the lab scale using appropriate methodologies and characterised using standard analytical techniques to ensure a consistent product was produced. The synthesis of each target product SRM 100-109 was carried out on a 20 g scale and samples sent for curing trials.

Lab-scale rubber compounding trials were undertaken in three phases:

The first phase of work involved testing many existing types of accelerator in CR compounds in order to build up a thorough knowledge of their effects on cure and to enable input into the QSAR modelling. Some of these have been used in CR previously and some have not. Both single accelerators and combinations of accelerators were tested. Additionally other chemicals, such as sulphur, were used in some formulations to assess their effect on cure.

The second phase involved obtaining benchmark data for ETU so that comparisons can be made between it and the new SafeRubber molecule later in the Project.

Phase three consisted of testing all of the newly synthesised replacement molecules to assess their suitability for ETU replacement. At the conclusion of phase three, two molecules were identified as potential candidates suitable for up-scaling.

Laboratory scale industrial rubber processing and testing equipment was used throughout the trials. To obtain the maximum value from the trials, it was essential that variables between batches were minimised wherever possible. To provide a consistent baseline material for the laboratory trials, a 20 kg batch of masterbatch was mixed in one lot by Clwyd Compounders, using its production equipment. Although each trial batch still had to have the different accelerators added to it individually, this method reduced the risk of deviation due to inconsistent weighing of the core ingredients and variations in mixing.

After mixing, each compound was tested on a Monsanto 100S rheometer to obtain its cure characteristics. Unless it was known from previous experience that a higher temperature was required for a particular accelerator, all test compounds were rheometer cured at 160°C to represent a typical industrial cure temperature. The remainder were cured at 175°C. When a compound proved to be capable of cure, test sheets and hardness slabs were then

compression moulded and sheets were used to provide dumbbell shapes for tensile and other testing.

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.

The first phase of compounding trials consisted of conducting a series of trials to establish the effects of a range of accelerators on the cure characteristics of a gumstock CR compound. Some accelerators were used in the masterbatch alone and some with the addition of a second accelerator or other curative. Along with others, all of the main rubber accelerator groups were represented whether or not they are generally used in CR compounds.

The information gained was used during the initial design of the new SafeRubber molecules. The effects of different molecular structures on the curing of CR could be assessed and taken into account when drawing up a shortlist of potential candidates. If a compound showed little or no cure, physical testing was not performed. In these cases, further trials were completed with higher concentrations of accelerator to establish whether or not they made a difference. To enable comparisons to be made between the new SafeRubber accelerator and ETU, a series of six compounds was mixed for use as a benchmark.

Synthesised accelerators were numbered SRM100 (SafeRubber Molecule 100) upwards for identification purposes. As with the compound numbers, the nomenclature carried no further implication. SRM102 and SRM104 both showed reasonable cure characteristics, with SRM102 being the best, in that it is cured quicker with a more distinct plateau than the slight marching modulus of SRM104. The rheometer trace for SRM102 is comparable to that of ETU.

Both SRM102 and SRM104 were chosen for scale up trials; however the synthesis of these molecules was complicated and accompanied by the formation of several by-products. As a consequence a new, reproducible procedure for the preparation of the target products SRM102/104 on a 1 kg scale as one batch syntheses was developed. The reaction conditions, reagents, solvents, temperature and reaction time were optimised. All intermediates, by-products and final products were analysed by ¹H NMR spectroscopy. The purity of the key intermediate and products SRM102/104 was analysed by HPLC-MS technique and acid-base titration analysis.

A new, scalable and reproducible method for the preparation of the intermediates was elaborated. All possible alternative methods and by-products were examined, analysed and optimal conditions found.

The intermediates and the optimal reaction conditions of the target accelerators SRM102 and SRM104 have been determined. The purity of synthesised products: intermediary, SRM102 and SRM104 was analysed using a HPLC technique and acid-base titration analysis.

Under standard conditions HPLC-MS analysis is not very reliable. There is the possibility that the analytes can interact with sorbent or mobile phase. The greatest problem is pH of the eluent: exchange of eluent to pH>9 will result in even lower sensitivity. The use of high pH values and various salt additives will result in extremely low lifetimes of HPLC standard columns. A detailed report explaining the synthesis route was written.

The bulk synthesis compounds was analysed and the results compared to the compounds synthesised at small scale. Analysis showed the compounds to appear chemically identical. To ensure curing efficiency was also maintained, bulk SRM102 and SRM104 samples were used in chloroprene curing experiments and the results compared to small-scale-synthesised SRM102 and SRM104 chloroprene cure curves. These are shown in Figure 1 below.

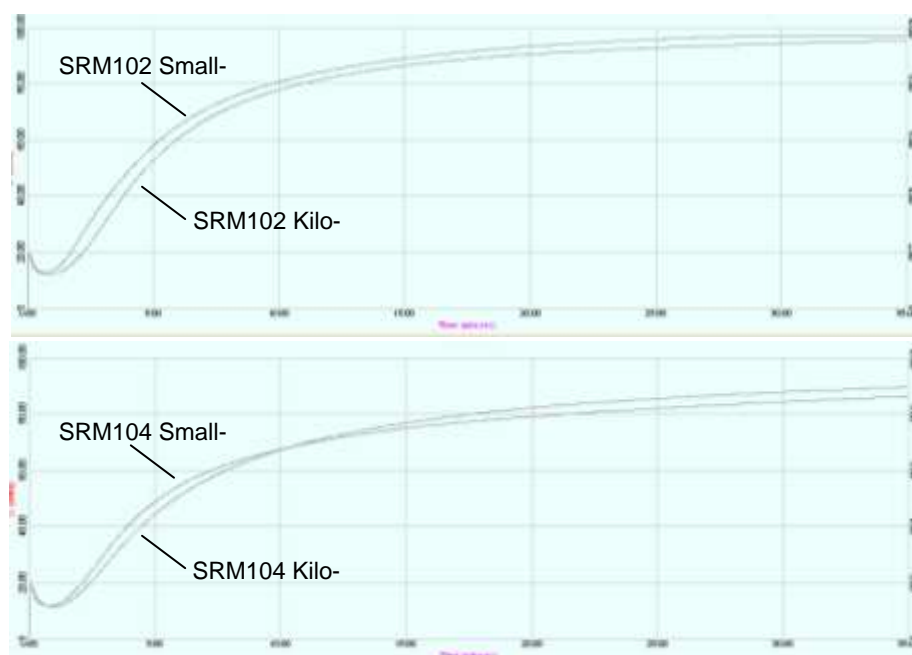


Figure 1. Comparison of chloroprene cure curves for kilo- versus small-scale-produced SRM102/104

It was clear from the cure curves that Kilo Lab produced samples of SRM102 and SRM104 have been successfully produced at Kilo Lab scale and shown to behave in the same way as samples produced at small scale in the curing of chloroprene rubber.

QSAR (Quantitative Structure Activity Relationship) has been an important study in the second year of the SafeRubber project in the understanding of the toxicological implications related to the introduction of new accelerator molecules. The outcome of a systematic QSAR study by UNIMIB based on 9 chemical scaffolds coupled with proposed molecules from rubber experts in the consortium was 15 molecules and 12 molecules were predicted to be safer than ETU. The QSAR investigation has only considered the toxicological and ecotoxicological properties and has not made any assumption on the curing properties. Based on the on-going curing tests two molecules, SRM 102 and SRM 104 have shown very promising results. Both molecules have been predicted to be not mutagenic, not carcinogen and not skin sensitizer. However based on the laboratory trials SRM 102 was chosen to be the best molecule for further development. Period 2 has been too early to apply for eventual animal tests.

QSAR has been a very important part of Period 2. The entire set of ca. 52.000 molecules in the OECD QSAR Toolbox has been considered initially by UNIMIB. By use of several “filters” the end result was the earlier mentioned 15 molecules. A number of QSAR tools have been selected to get prediction of carcinogenicity, mutagenicity, developmental toxicity, acute toxicity, skin sensitisation, bioaccumulation and biodegradability. QSAR tools designed to meet REACH requirements have been used. Such tools are OECD QSAR Toolbox, CAESAR, ToxTree, T.E.S.T. and Lazar.

Important criteria to meet when using QSAR are:

1. Results are derived from a QSAR model whose scientific validity has been established
2. The substance falls within the application domain of the QSAR model
3. Results are adequate for the purpose of classification and/or risk assessment
4. Adequate and reliable documentation of the applied method is provided
5. In cases where there is uncertainty related to one or more information elements, QSAR

QSAR (quantitative structure activity relationship) methods were applied in order to analyse how molecular structure of chloroprene rubber accelerators relates to their rheological and mechanical properties. QSAR models were developed in order to disclose which structural features mainly affect the mechanism of vulcanization. Regression mathematical models were developed for two rheological properties (Scorch time and Optimum cure time), and three mechanical properties (Modulus 100%, Hardness and Elongation at break). QSAR models were calibrated using experimental values of fourteen accelerators belonging to diverse chemical classes. A structural interpretation of each QSAR model was given, drawing hypotheses on the correlations between specific structural features and the analysed rheological and mechanical properties as well as defining possible chemical patterns connected to the mechanism of vulcanization.

HSE and REACH

A robust desk based review of toxicity of the molecules for the SafeRubber novel accelerator system for polychloroprene and associated rubbers inclusive of: Adherence to legislation (REACH, COSHH); Sustainability benefits and Health and Safety of workers has been carried out. This has so far been focused on ETU as a reference for the new accelerator system under development. Ethylene thiourea (ETU) has been used as accelerator in production of chloroprene rubber for decades. ETU is classified as CMR (Carcinogenic, Mutagenic or Toxic to Reproduction) and is thereby a substance that could identified as a Substance of Very High Concern and afterwards included in Annex XIV of REACH (Authorisation). The main purpose with REACH is to ensure a high level of protection of human health and the environment.

From the desk-based review of toxicity the key message is that ETU, the present used accelerator, has been classified as Reproductive toxicant category 1B with Hazard statement H360D – may damage the unborn child. Being classified as CMR, ETU is a substance that could be identified under REACH as a Substance of Very High Concern (SVHC) and therefor a potential candidate to be included in the Candidate List and later in Annex XIV of REACH (Authorisation).

Hazardous substances will be subject to Authorisation or Restrictions to ensure safe use. Authorisation is a complex and weighty process. Relevant substances need to go through a process before they eventually are included in Annex XIV:

1. Identification of SVHC: Member States (MS) or ECHA on behalf of the Commission include the substance in the Registry of Intentions
2. Submission of REACH Annex XV dossiers
3. Publication of Annex XV reports for comments
4. Development of Support Document (incl. responses to comments) by MS and ECHA
5. Agreement on identification by ECHA's Member State Committee (if comments are received)
6. Inclusion in "Candidate list"

7. Immediate obligations following inclusion in the 'candidate list' for substances, mixtures or articles containing a "Candidate list" substance

The last substances were included in the "Candidate list" on 20.06.2011 and the list contains now 53 substances. The first 6 substances for Annex XIV was published 17.02.2011 and a corrigendum was issued the day after (Regulation (EC) No. 143/2011).

Article 67 in REACH states that "A substance on its own, in a mixture or in an article, for which Annex XVII contains a restriction shall not be manufactured, placed on the market or used unless it complies with the conditions of that restriction". ETU use is currently restricted due to its classification as "toxic to reproduction category 1B": Such substances shall not be placed on the market, or used, as substances, as constituents of other substances, or, in mixtures, for supply to the general public when the individual concentration in the substance or mixture is equal to or greater than: either the relevant specific concentration limit specified in Part 3 of Annex VI to Regulation (EC) No 1272/2008, or the relevant concentration specified in Directive 1999/45/EC.

QSAR has been important in the SafeRubber project to screen for potential safe substances and to demonstrate that selected accelerator candidates are safer than ETU. The main purpose of QSAR was therefore not focused on REACH registration.

The outcome of a systematic QSAR study by UNIMIB was that 6 substances were predicted to be not mutagenic, not carcinogen and not skin sensitizer. Of these substances SRM 102 was selected based on its curing properties as an accelerator for polychloroprene.

The REACH Regulation mentions (Q)SARs as a mean to provide data without doing animal testing. ECHA (European Chemical Agency) presented a paper in 2009 informing that results of QSAR may be used instead of testing when the following criteria are met:

1. Results are derived from a QSAR model whose scientific validity has been established
2. The substance falls within the application domain of the QSAR model
3. Results are adequate for the purpose of classification and labelling and/or risk assessment
4. Adequate and reliable documentation of the applied method is provided
5. In cases where there is uncertainty related to one or more information elements, QSAR results may still be used in the context of a Weight of Evidence approach

The main challenge with SRM 102 regarding QSAR is that this substance is ionic in nature. Due to this the following actions were taken:

- A screening of commercial tools able to handle QSAR predictions on disconnected structures was performed, but all the considered QSAR tools (ACDLAB - ACD/Tox Suite, Simulation plus, Accelrys - Discovery Studio TOPKAT) cannot support disconnected structures
- Queries on the databases of the OECD QSAR Toolbox were carried out in order to find disconnected structures to be used for read-across models. However few experimental data were available in this area and then mainly for different endpoints, organisms and test conditions, making them not comparable and suitable for making predictions. Therefore, the set of disconnected structures in the QSAR toolbox was considered not significant in order to enhance reliable read-across models
- Relevant papers published in the scientific literature reporting QSAR models on disconnected structures were not found

In practice this means that our QSAR data should be used as supportive data for REACH registration. This means that the needed data in REACH Annex VII should be based on test data. Norner is overseeing REACH testing which started testing at the end of February 2013 based on a sample of SRM 102 made in Robinson Brothers Ltd.'s pilot plant. Tests are still ongoing. The results so far have shown that SRM 102 is safe and the test data confirms QSAR predictions on toxicity.

As part of Annex VII testing for REACH registration (volume 1-10 t/y) and also Article 26 notification to ECHA is important. This work is currently on-going.

Towards the end of the SafeRubber project ECHA announced in the "Registry of current SVHC intentions" that Sweden has filed a "notification of intention" of ETU (scope CMR) on the 16th April 2013. A likely consequence of this is that ETU will be included in the Candidate List during 2013.

LIFE CYCLE ASSESSMENT

The following four steps were defined for making a Life Cycle Assessment (LCA) according to ISO 14040 for replacement of ETU by SRM102 as accelerator in the production process of chloroprene rubber:

1. Goal and scope definition

The objectives for doing the LCA comparison between SRM102 and ETU are:

- Better understanding of the value chain
- Insight into potential environmental impact risks
- Aligned economic, environmental and societal goals
- Engagement of value chain partners and stakeholders
- Identification of effective improvements

2. Inventory Analysis, including tracking material and energy flows in all relevant process steps:

This is an important part, especially to collect the right information with respect to worker exposure and risk scenarios, and influence on the environment during accelerator production and vulcanization of chloroprene rubber, in addition to distribution, use and waste generation.

3. Impact Assessment

For the Impact Assessment in this project it has been decided to use ECETOC TRA (Targeted Risk Assessment) as offered by European Centre for Ecotoxicology and Toxicology of Chemicals (www.ecetoc.org). However data are too few for a comprehensive TRA to be performed at this stage.

An additional requirement was to try to reduce the heavy metal content (ZnO) of the compound and also to carryout leaching studies.

Reduction of heavy metal oxides

Polychloroprene rubber (CR) is commonly cross-linked by adding a combination of Zinc oxide (5 parts per hundred rubber (phr)), magnesium oxide (4 phr) and an

accelerator such as ethylene thiourea (ETU) or the new SafeRubber molecule, SRM102. Additional accelerators may be used to boost the cure rate.

According to the EPA “zinc ion can become available from zinc oxide through several mechanisms” and that “Zinc ion can reasonably be anticipated to be toxic to aquatic organisms”. One of the wider European benefits anticipated by the Safe Rubber Project is a reduction in the use of Zinc Oxide.

Two different experimental approaches were evaluated a) the replacement of ZnO by TiO₂ and b) the replacement by a Multi-Functional Additive (MFA)

TiO₂

A literature and patent search to identify previous work conducted with TiO₂ was undertaken. It was identified that titanium dioxide has been used as filler in numerous elastomeric formulations but the use of this compound as a curing/vulcanising agent, in its own right (there are patents relating to titanium dioxide-containing complex organic molecules and titanium dioxide photocatalysts), is extremely limited (no patents were found for its use in polychloroprene formulations). However, a reference from this search was identified:

16/9/3. 'Room temperature curable silicone rubber composition for use in e.g. electric appliance, composition comprises silicon polymer, surface treated silica, silane adhesive, silicone oil and titania type or zirconium-based curing catalyst'

Initial tests using TiO₂ were performed at an early stage in the SafeRubber Project as part of a wider series of trials in conjunction with work investigating the curing mechanism of CR and also to provide data for QSAR computer modelling. When it was realised that TiO₂ had the potential to replace zinc oxide (ZnO), it was decided to perform further work.

Five formulations were mixed and rheometer tested to establish their cure characteristics. A measure of cure efficiency was established by deducting the minimum rheometer torque from the maximum. It was decided to investigate whether CR could be cured using TiO₂ in place of ZnO using ETU as an accelerator with the addition of sulphur to the formulation and a good state of cure was obtained.

The optimum quantity of TiO₂ was then investigated. Three compounds were formulated using different phr of TiO₂. These were based on an alternative accelerator system.

The final stage of work conducted during the Project was to investigate the effects of a reduction of sulphur and the combined metal oxides, in particular zinc oxide, or titanium dioxide, and magnesium oxide.

The compounds were mixed and tested for their cure characteristics using a rheometer and for their physical properties. The following conclusions can be observed from the trials:

1. SRM102 gives a better cure than ETU, both in cure efficiency and physical properties.
2. A reduction of 1phr of each of the two metal oxides in the SRM cure compound does reduce the state of cure and physical properties; however the results are broadly in line with the ETU cured compound.

3. Reducing the sulphur content from 1 phr to 0.5 phr (active) at the same time as reducing the metal oxides does not greatly affect the cure.
4. If the sulphur is removed completely, reasonable cure efficiency is obtained but the physical properties drop considerably.
5. **It is possible to replace zinc oxide with titanium dioxide** in the curing system of polychloroprene rubber compounds.
6. It is possible to reduce the quantity of metal oxides from the current 5 phr ZnO and 4 phr MgO without greatly affecting the physical properties of the cured compound.

However there is still a great deal of further work which could be conducted, especially on the subject of ZnO replacement. The proportions of metal oxides and other components of the curing system all require optimisation and a full suite of physical testing needs to be performed once this is done, this work will continue post project.

Multi-Functional Additive (MFA)

A small amount of multi-functional additive (MFA) was synthesised to test whether it was possible to reduce the level of ZnO in a CR formulation. Mechanical tests have been completed with tensile testing results done after curing for 1.5 times T90. Results including tensile modulus at various extensions, ultimate tensile strength and elongation at break were found. Similarly MDR cure results for a 15 minute test at 160 °C were found including maximum torque reached (MH), scorch time (TS1) and maximum cure rate.

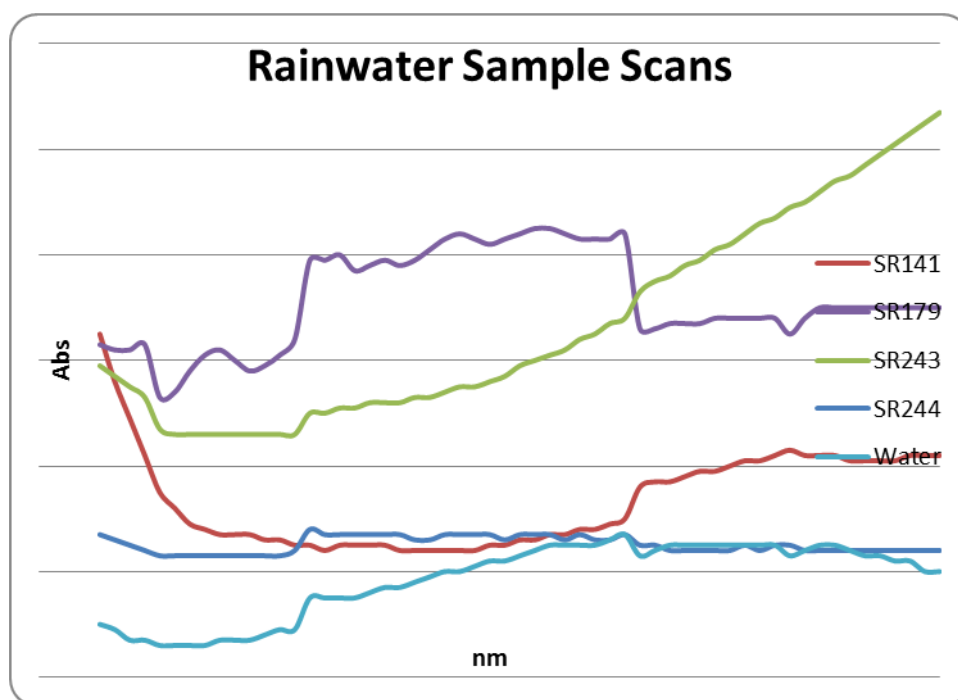
The physical testing results show that the standard cure system produces similar results to the SRM102 containing systems, in regard to both tensile results and cure results.

The conclusion from this small trial indicates that by incorporating MFA into a cure system it is possible to reduce the level of ZnO. It is recommended that partners who wish to use MFA carryout further optimisation work post project.

Leaching tests

In order to assess leaching of components of chloroprene rubber into rainwater over time, and thus assess environmental impact, a leaching experiment was set up. Samples of known weight (5g) of chloroprene rubber with different compositions were rinsed with rainwater and then placed into 25ml of rainwater and left for 12 weeks, with occasional stirring. This set-up aimed to mimic at a basic level the environment in a landfill or similar waste disposal site. After a 12-week period, the water samples were examined using UV-vis spectrophotometry to determine if any leaching of material had occurred.

The results from the UV-vis spectrophotometry analyses are shown in Figure 2.



SR141 = ETU Gumstock; SR243 = ETU black; SR179 = SRM102 Gumstock; SR244 = SRM102 Black

Figure 2. UV-vis data for rainwater samples after 12 weeks in contact with chloroprene rubber samples.

As can be seen from the data, absorbance for all samples is very low. For the chloroprene gumstock sample cured with SRM102, no leaching of any components is observed after 12 weeks. For the other samples, absorbance values are all below 0.09, indicating exceptionally low concentrations of leached components. The lack of defined peaks also suggests the absorbance values observed are more likely to be down to light scattering by fines in the rainwater and machine error than due to absorbance by dissolved components.

Different samples of chloroprene rubber were suspended in rainwater for 12 weeks and the water subsequently analysed by UV-visible spectrophotometry. Data obtained suggest that leaching of the component chemicals into the rainwater over the 12 week period is minimal and does not provide an environmental risk.

UV testing

UV testing was carried out on compounds made from ETU and SRM102 according to EOTA (European Organisation for Technical Approvals) Technical Report which specifies exposure procedures for artificial weathering using EN ISO 4892

The radiant exposure range in Northern Europe is typically 128MJ/m² per year.

The laboratory light source type 1 (UV-A 340 nm peak) was used where radiant emission below 400 nm makes up at least 80% of its total light output and where radiant emission below 300nm is less than 2% of its total light output, with a spectral irradiance of (45 ± 10) W/m² in the bandpass of 300 nm to 400 nm. Figure 3.

The simulation exposure conditions were for a moderate climate in Europe. The testing cycle was UV radiation for 4 hrs at 60°C then a condensation cycle for 4 hrs at 50°C then repeated. The lamps run at ~40W/m² (300-400nm). Testing was for 500 hours, this is equivalent to half a year in the Arizona desert.



Fig 3. UV cabinet according to EOTA (European Organisation for Technical Approvals) Technical Report which specifies exposure procedures for artificial weathering using EN ISO 4892

The test samples were black filled and gumstock moulded compounds and the results show that there is no difference between compounds made with ETU and SRM102 and both show that there is negligible degradation due to UV radiation.

4. Interpretation

The interpretation including limits, gaps, recommendations and conclusions will be made after the TRA has been finalized. However, chloroprene compounds containing SRM 102 have been tested in a wide array of industrial processing techniques in five factories in three different countries. In every case SRM102 has equalled or exceeded compound containing ETU. Some findings from these tests relevant for environmental impact are

- In line with the experience with the vulcanization trials, the ability to flow and fill easily the mould has been found to be much better in the CR rubbers made with SRM102 than in the standard ones. This could arise in a reduction of the mass of rubber needed to vulcanize a piece which in turn will reduce the scrap.
- The cure cycle could easily be reduced through optimisation of the accelerator system.
- ZnO is very toxic to aquatic organism. It is possible to reduce the level of ZnO, by using either TiO₂ or MFA's especially when SRM102 is used as the accelerator; however further trials post project will be needed to investigate other effects such as ageing and oil resistance etc.
- Rubber samples have been placed into rainwater. After 12 weeks samples look similar. However, algae growth on samples produced by use of SRM102 suggests they're not toxic!

More detail on the industrial validation trials is given below.

SCALE UP

Further studies carried out by the Research Partners on the two potential candidates have shown that SRM102 gives improved rheological and physico-mechanical properties over SRM104. As a consequence, the Consortium agreed that scale-up should concentrate on SRM102 only. A series of validation trials were carried in order to ascertain the robustness of

the process and to obtain the critical Health and Safety data for the process before proceeding to Pilot Plant scale.

The scale-up was carried out at Robinson Brothers Ltd, which is ISO14001 registered (Certificate No: EMS 57413).

Data needed to make an Impact Assessment are:

- General physicochemical data of SRM102 and ETU (molecular weight, vapour pressure, water solubility, partition coefficients, in addition to results from biodegradability testing).
- In general, the routes of potential human exposure to SRM102 (and ETU) are inhalation, ingestion and dermal contact and the potential occupational exposure is greatest for workers involved in the manufacture of the accelerator and the manufacture of rubber and rubber products. Data needed for the worker exposure and risk scenarios (physical form, vapour pressure and operating temperatures). In addition information on ventilation, the use of respiratory and dermal protection to calculate inhalation exposure and dermal exposure are needed.
- Data on energy inputs (track quantity, type and source of energy).
- Data on production output including purity and eventually by-products.
- Data on emissions and waste.

The quality of SRM102 manufactured by Robinson Brothers Limited in their pilot plant has been shown to be comparable to the sample synthesised by Grand Synthesis Latvia based on performance usage tests in CR but appears to contain less contaminants based on DSC-TGA and has a smaller, more uniform particle size.

SRM102 was supplied to Clwyd Compounders, MGN, Mixer and MaTRI for their own industrial compounding optimisation trials. These trials have been very successful; please see below for more detailed information.

INDUSTRIAL VALIDATION TRIALS

The Consortium developed a test matrix, shown in Table 1, which included the types of process, types of product and partners with the capability to perform the industrial validation trials. It was evident that the Consortium did not have the capability to perform all of the necessary processes. Two companies outside the Consortium offered to provide their assistance with the trials on the basis that the aims of the Project offer great potential to improve safety in the European rubber industry in the future.

The two external partners were:

- 1) *Nufox Rubber Limited*
Unit 1 Bentley Avenue
Middleton
Manchester
M24 2GP
United Kingdom
- 2) B D Technical Polymer Ltd
Unit 202B, Cooks Road
Weldon North Industrial Estate

Corby
Northamptonshire
NN17 5JT
United Kingdom

Safe Rubber Industrial Trial Test Matrix			
Process	Application		Performing Partner
Extrusion	Autoclave cure	Round section	Nufox Rubber* (Supervised by MaTRI and Clwyd)
		Garvey die section	Mixer
	Continuous cure	Round section	Nufox Rubber* (Supervised by MaTRI and Clwyd)
		Polychloroprene cable sheathing Type 5GM3	Mixer
Moulding	Compression	Thin sections	MGN
		Thick sections	MGN
		Rubber to metal bonding	MGN
	Injection moulding	Various	BD Technical Polymer* (Supervised by MaTRI)

*Non-Consortium Member

Table 1. Industrial Trial Test Matrix

Notes:

- As both compression moulding and injection moulding trials were successful, transfer moulding was deemed by the Consortium rubber experts to be un-necessary because it is a hybrid of the two processes.
- Calendering was not trialled on the grounds that it would require a large quantity of compound along with lengthy machine set up times and as such was too expensive. Furthermore the rubber experts in the Consortium agreed that if the extrusion trials were successful, then there would be no reason why calendering would not also be successful.
- Polychloroprene sheathing trials were performed using a specially developed compound to meet industry specifications. This utilised a cross-head extruder.
- Two types of continuous cure were trialled: infra-red and salt-bath.

MaTRI provided all partners with guidance and health and safety information. The technical guidance was taken from work performed with SRM102. The health and safety information was based on work by GSL.

The injection moulding trial was considered to be a success. No moulding defects were observed, the compound cured after the mould was fully loaded and there was no indication of premature cure (scorch) occurring. The 15 minute cure cycle could easily be reduced either through optimisation of the accelerator system or by using increased temperatures. The products obtained were of equal quality to products made using traditional ETU accelerated compound.

Two types of continuous cure or vulcanisation (CV) were trialled with compound containing SRM102; salt-bath and infra-red. Both methods use a normal cold feed extruder, the main difference being the method by which heat is provided to the un-cured profile.

Salt bath CV is a commonly used liquid curing method for extrudates. CV is frequently chosen for producing products such as tubing, hoses and weather stripping. Salt baths are relatively short-length curing units because salt has good heat exchange properties and can be used at high temperatures of up to 260°C. Salt does not cause surface oxidation, and is easy to clean off the finished product using water.

Infra-red (IR) CV lines use a row of IR heaters to cure the extrudate and tend to be longer because heat flow into the rubber compound is slower when compared to a salt bath.

In both processes it is essential that the compound starts to cure enough to maintain its shape before distortion due to melting occurs. Another consideration is the formation of porosity which can be caused by the formation of volatiles before cure has taken place. It can also be caused by moisture in the compound turning to steam.

Continuous cure trials were performed by Nufox Rubber on both its infra-red and the salt-bath extrusion lines. Autoclave cure trials were also carried out by Nufox.

The compound was extruded through a 10mm circular die and various parameters were changed during the course of the trials until optimum conditions were obtained.

Whilst it cannot be considered as continuous cure, samples of extrudate were taken from the extruder line and cured in an autoclave. This process consists of placing the un-cured extrudate on a talc covered, aluminium tray in an atmosphere of pressurised steam. The pressure used for the trials 4 bar which equates to 152°C.

Mixer is a manufacturer of rubber and thermoplastic compounds for the insulation, sheathing and filling of flexible cables rubber cables, power cables and flame-retardant cables. This is a specialist market due to the use of highly specified material with high volumes and low margins, making it different from the general purpose rubber goods industry.

Mixer's task in the SafeRubber project was to validate the use of the new accelerator SRM102, in an industrial manufacturing environment and test the substitution of ETU in rubber cables, the overall aim being to reduce the toxicity caused by fumes from ETU during manufacture without losing technical performance.

All the experiments performed by Mixer show that SRM102 could be an effective replacement of ETU in polychloroprene based compound. Crosslinking density, hardness, scorch safety, mechanical properties and more importantly, ageing resistance are very close to what could be obtained with ETU.

An extruder was fitted with a Garvey die to test the extrusion properties because it was felt that this would highlight any problems such as scorch. It was identified that there is little or no difference between the two compounds.

In conclusion, it can be stated that there is no discernible difference between the processing characteristics of compound containing ETU or SRM102. Both extruded in an identical manner with no problems or issues.

Clwyd Compounders Ltd. was also required to carry out industrial evaluation studies on the use of SafeRubber accelerators SRM102 in polychloroprene rubber compounds. They concluded that for both general purpose and high-quality SRM102 compounds show good basic properties. The high-quality CR compound is within reach of the challenging DTD 5514 specification requirement, which has traditionally required the use of ETU containing

compounds. Although SRM102 containing general purpose CR compounds show low elongation compared to other accelerator systems, tensile strength and modulus at 100% elongation are higher. Compression set and fluid resistance testing showed comparable results to the standard accelerator systems, suggesting that a good state of cure is achieved in a general-purpose CR compound using 1 phr of SafeRubber accelerators.

Clwyd also carried out a number of extrusion trials and concluded that the trial compounds generally extruded well at a speed of 2.5m/minute and could also be cured using an autoclave cure. The addition of 6 phr of Caloxol and 1.5 phr SRM102 to the polychloroprene masterbatch enabled the compound to be cured in a salt bath at 230°C without having a significant detrimental effect on the scorch safety of the compound. Nufox reported that this is the first time that they have successfully cured a CR extruded cord in the salt bath.

MGN's role was to validate the use of SRM102 in moulding compounds in an industrial environment, specifically compression moulding of various sized parts and rubber to metal bonding. MGN does not possess any injection or transfer moulds. MGN selected some pieces currently manufactured by the company with chloroprene rubber in production moulds, in order to test the whole range of applications described earlier. They carried out trials on five different parts.

1. Guiding part for elevators. In this case, the rubber should also present a very good adhesion to the metallic parts, as this is a core requirement for this piece.



2. Draught excluder. The most important peculiarity of this piece is its reduced thickness, compared with the other two dimensions. In this case, the rubber should flow well enough when closing the mould, to fill it completely. Otherwise, air bubbles or lack of material could be observed in certain areas of the final product.



3. Bellows. In this case, the main particularity of the piece is its wavy shape, what makes the extraction from the mould a critical process. The rubber shouldn't present fragility when still hot, otherwise extracting the piece from the mould without harming the piece would be impossible.



4. Elastic support. In this case, the main issue in the vulcanization process is that the rubber of inside the piece has to vulcanize completely.



5. Elastic coupling. In this case, the rubber should also present a very good adhesion to the metallic parts.



MGN found that the best characteristic observed in these new rubbers was the capacity of the rubber to fill the mould. This means that less rubber is required resulting in less scrap to be disposed of.

To conclude chloroprene compounds containing SRM 102 have been tested in a wide array of industrial processing techniques in five factories in three different countries. In every case SRM102 has performed as well as, or better than compound containing ETU. It has proved itself to be a viable replacement for ETU as an accelerator.

COMMERCIAL VIABILITY

The rubber manufacturing trials have proven that the SRM102 is also a commercially feasible replacement for ETU.

All industrial validation trials carried out during the project indicate that the proportion of SRM102 used in the formulas for all the end users will be very similar to ETU i.e. around 1%, therefore the current price estimates of the accelerator SRM102 are not anticipated to increase the manufacturing cost of a final rubber compound more than 105% of the equivalent compound made using ETU.

DISSEMINATION

Dissemination has been active throughout the project and high visibility achieved for project partners and project results resulting in:

- More than 41 press quotes
- 9 articles in rubber technology & science magazines (1 peer reviewed) + 1 master thesis dissertation
- 4,890 unique visitors of the project website until May 2013
- More than 200 unique visitors/month of the project website
- Dissemination of information by consortium members at 61 EU and global rubber industry events (conferences & trade fairs): 832 participants at conferences and a potential of 700,000 trade fair visitors

- Presentation of project results at 5 Rubber Technology and 2 Chemometrics seminars in UK, Belgium, France and Italy.
- Training achieved of all project partners on the dissemination of the project results by the interactive development of a Dissemination Presentation Tool

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