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Analysis of an Adhesion Promoter for Rubber to Metal Bonding

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Analysis of an Adhesion Promoter for Rubber to Metal Bonding

By

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A thesis presented to

Dublin Institute of Technology for award of Ph. D

Prepared under the supervision of

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Abstract

The intermolecular and intramolecular changes induced by thermal stress in an industrial rubber to metal coupling agent (the ‘green molecule’ or GM) are the subject of this thesis. The GM was analysed *in-situ* in a model application environment using vibrational spectroscopy. NMR spectroscopy was used in order to analyse the solution chemistry of the compound and how this changed as a result of thermal stress. The interaction of the GM and the substrate was analysed using a range of surface analysis techniques including XPS, AFMIR and EDX. An example of a complex substrate, the zinc phosphate conversion coating, was analysed using vibrational spectroscopy and EDX to determine the manner in which it behaves in the application environment. The effect of the industrial application environment was examined by preparing adhesion test pieces and analysing the manner in which the application temperature affected their performance. In tandem with the adhesion testing, the interaction of the substrate, the GM and the rubber in the application environment was examined. This was done by preparing test pieces that used the GM in isolation as the intermediate in rubber to metal bonding. It is typically used in a formulation. Stability testing of the GM in DMSO was carried out.

Vibrational analysis of the GM revealed that urethane hydrogen bonding was playing an active role in directing the intermolecular state of the GM as a function of temperature. This intermolecular association was seen to have an effect on the manner in which the GM hydrolysed and condensed in the model application environment. Solution NMR of the GM before and after being subjected to thermal stress revealed that the GM was resistant to thermally induced hydrolysis at high concentration. This effect was a result of the urethane hydrogen bonding identified using the vibrational analysis. Surface analysis of mild steel substrates that were exposed to the GM at high temperature
showed that the GM binds to the substrate very sparingly. The mirror polished mild steel surfaces were visibly unchanged after thermal treatment in the presence of the pure GM. XPS analysis gave the only indication that any of the GM had bonded to the surface. IR analysis showed that the Henkel ZPCC dehydrated when subjected to thermal stress. EDX of thermally treated ZPCC showed that oxidation was occurring at the ZPCC coating however it is unclear whether this oxidation was occurring to metallic species contained in the coating or to the steel substrate underneath the coating. Adhesion testing showed that the rubber to metal adhesive formulation containing the GM formed stronger adhesive joints between the rubber and the metal at lower processing and curing temperatures than those typically used in industry. Analysis of test pieces prepared using the GM as the sole intermediate between the rubber and the metal showed that the GM nitroso moiety reacted upon mixing with the rubber. This interaction between the GM and the rubber was accompanied by sulphur release from the rubber which deposited as a sulphate on the iron substrate. The morphology of the sulphate deposit was temperature dependent, changing from crystalline to amorphous as the sample preparation temperature increased. Stability testing, where the hydrolysis of the GM induced by minute concentrations of water in DMSO-d6 was compare with common alkoxyisilane precursors GPTMS and MAPTMS, showed that the GM was relatively stable in comparison to the alkoxyisilane precursors that did not possess a urethane moiety in their molecular structure. The GM structure incorporates a urethane moiety that acts to stabilise the GM thermally and chemically. The hydrolysis and condensation behaviour of the GM is novel in comparison to common alkoxyisilane precursors. The incorporation of the urethane moiety in the design of novel alkoxyisilane precursors and also the preparation of urethane functionalised analogues of common organofunctional alkoxyisilane
compounds may open a doorway to improved alkoxysilane based surface treatments. These treatments will also be more easily ‘tuned’ to meet the requirements of a given application.
Declaration

I certify that this thesis, which I now submit for examination for the award of PhD, is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my own work.

This thesis was prepared according to the regulations for graduate study by research of Dublin Institute of Technology and has not been submitted in whole or in part for another award in any other third level institution.

The work reported on in this thesis conforms to the principles and requirements of DIT’s guidelines for ethics in research.

____________________

Killian Barton

22\textsuperscript{nd} September 2016
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Chapter 1: Introduction

1.1 Adhesion Promoters in Industry

Adhesion plays a critical role in the application of surface treatments. Primers, conversion coatings, paints and adhesive joints depend on a satisfactory adhesive interaction between the treatment and substrate in order to be deemed effective. The substrate must be prepared carefully before any treatment is applied as its chemical composition, morphology, roughness and cleanliness are all factors that will impact on interfacial adhesion. Similarly, the chemical composition of the treatment, its viscosity and the technique used in its application to the substrate must be considered. In cases where the adhesive interface comprises chemically incompatible materials, e.g. an organic polymer applied to a glass substrate, adhesion promoters may be applied.[1] Alkoxy silane, titanate and zirconate coupling agents are commonly used to improve the compatibility between inorganic and organic materials in industry. [2] In the context of this project, the chemical composition and reactivity of alkoxy silane coupling agents is relevant and a thorough presentation of these themes is presented in sections 1.4 and 1.5.

1.2 The Henkel Green Molecule

The Henkel green molecule (GM) is an adhesion promoter included in a rubber to metal adhesive formulation (Figure 1.1). It is intended for the application of bonding natural rubber (NR) to inorganic substrate surfaces. Examples of these surfaces include mild steel and zinc phosphate conversion coated mild steel. The advantage of the GM containing formulation is that it eliminates the need for a primer prior to application of the adhesive and hence is more efficient. The GM is also a non-toxic compound and this
is an advantage given the pressure on industry to eliminate the use of hazardous substances. The compound is comprised of three chemical functionalities:

- An alkoxy silane moiety for adhesion to the inorganic surface (red)
- A urethane moiety for chemical stability (blue)
- A nitroso moiety for adhesion to the natural rubber (green)

![Compound Structure](image)

Figure 1.1: The GM nitrososilane coupling agent.

The intended mechanism of action of the GM is that it should act as a bridging molecule, covalently connecting the incompatible inorganic and organic interfaces. The formulation containing the GM is applied to the substrate and allowed to dry before bonding. In the case of bonding directly to steel, the part will be cleaned and roughened using a grit blast. This process can be overlooked in the case of bonding to zinc phosphate conversion coated surfaces. The part to be bonded is then introduced to the NR through an injection moulding process. During the injection moulding process, bonding and curing of the rubber are carried out simultaneously.[3][4]
1.3 Rubber-to-metal Bonding

Figure 1.2: Examples of products that rely on rubber to metal bonding. Clockwise from top left: vibration dampers, bushes, bridge bearings and steel cord reinforced tyres.

The industrial importance of rubber-to-metal bonding is well known. Rubber-to-metal assemblies are used at joined interfaces where strength and flexibility are required in order to cope with dynamic stresses (Figure 1.2). Examples include engine mountings, helicopter rotor bearings, bridge bearings, torsional dampeners, flexible couplings and suspension bushings. [5] There are many approaches to bonding rubber to metal and a selection of them will be outlined.

The steel substrate may be treated with a layer of ebonite prior to bonding. Ebonite is natural rubber with a high concentration of elemental sulphur inclusion, approximately ten times higher than that in the natural rubber to be bonded. The resulting bond has poor temperature resistance. The process is limited in the range of rubbers to which the ebonite treated substrate can be bonded.

Alternatively, the inorganic substrate may be electroplated with an appropriate alloy. This is a solution process where the steel component is incorporated as an electrode in an electric circuit and immersed in a solution containing the desired material or metal.
for deposition. A current is passed through the circuit and the component, acting as the cathode, reduces the metal ions in the coating solution and this allows for the formation of a metallic deposit on the surface of the component. Alloys containing antimony, copper, zinc, bismuth and arsenic have all been used however the most successful has been brass. Given that electroplating will generate different surface treatments depending on the process temperature, anode composition, plating current density, time and bath composition, it is apparent why widespread adoption of this method has not occurred. Nevertheless, electroplating of tyre cords with brass is a common manufacturing technique when preparing to bond rubber.[5]

Isocyanates have been used to prepare metal substrates for bonding. The advantage here is that the isocyanate treated metal may bond to a range of rubbers. The moisture sensitivity of isocyanato functionalised compounds requires that the substrate to be bound must be protected before bonding. Any interaction with moisture will result in a significant loss in bond integrity. This requirement reduces the convenience of use of isocyanate based adhesion promoters. [6]

Self-bonding compounds have been prepared that are comprised of the elastomer and an additive that binds well to the metal substrate. Additives include resorcinol, hexamethyleneimelamine and zinc salts of acrylic and methacrylic acid. This strategy of bonding metal to rubber is flawed in that the self-bonding compound presents a bonding surface not just to the surface but also to the die in the case of an injection moulding process. This results in bonding of the elastomer to the die which is obviously problematic during manufacturing. In addition, the self-bonding compounds have been observed to exhibit poor environmental resistance as a result of the incorporation of the adhesion promoter.[7]
1.4 Injection Moulding

Injection moulding is a common industrial process whereby components comprising rubber and metal are prepared. It is an in-vulcanisation bonding technique; adhesion of the rubber to the metal substrate and curing of the rubber are accomplished simultaneously. The surface of the metal component that is to act as the bonding interface with the rubber is cleaned, roughened and treated with an adhesive formulation prior to being fixed into a mould or die. The die containing the metal parts is heated to the temperature of the rubber curing step for a fixed period. After this prebake step, the rubber is injected into the die by a high pressure ram. The parts are then kept at a constant temperature for a fixed period of time to allow the rubber to cure. The duration of the curing step is inversely dependent on the curing temperature.[8]

1.5 Alkoxysilane Coupling Agents

The Henkel GM is designed to be a bridging molecule which covalently bonds to both inorganic and organic materials. The GM may be described as an alkoxysilane coupling agent (ACA) but also, and just as appropriately, as an organically modified alkoxysilane. The former nomenclature has its origin in the development of surface modification techniques for inorganic materials intended for use as reinforcing agents in polymers. The latter is that used for the same class of compound used in sol-gel science to prepare organically modified silicates. Although both names describe the same thing, the disciplines from which they originate diverge sharply on one critical aspect. Surface modification requires, ideally, a monolayer of the ACA to be deposited on the inorganic material surface thus forming a direct covalent bond. In order to do this, it is preferable to prepare the ACA so that it is in its silanol form. Sol-gel science is the science of
designing materials with novel physical, optical or chemical characteristics and may be described as a hybrid inorganic-organic polymer science. Therefore, the organically modified alkoxysilanes used in sol-gel science are prepared so that the silanol form is consumed by condensation reactions forming a polymer material. Research in both disciplines has elucidated many aspects relating to the chemistry of ACAs / organically modified alkoxysilanes and the fundamental aspects of this chemistry will be presented here.

1.6 The Chemistry of Organically Modified Alkoxysilanes

1.6.1 Hydrolysis

The formation of silanol groups on the ACA is essential if covalent bonds with a given inorganic material are to be formed. The general equation is given in (1).

\[(OR)_3Si - OR + H_2O ⇌ (OR)_3Si - OH + ROH \quad (1)\]

Tetraethylorthosilicate (TEOS) is a tetraalkoxysilane that does not include an organic moiety for crosslinking with organic polymers. Its reactivity reflects that of the alkoxysilane moiety and it is ideal for illustrating the effect of reaction conditions on hydrolysis.

Hydrolysis is carried out in the presence of water and, in the case of TEOS and alkoxysilanes in general with poor water solubility, a homogenising agent such as ethanol or methanol. TEOS will hydrolyse slowly in water at neutral pH and it is common practice to use acid or base catalysis to increase the rate of the reaction. Hydrolysis, for either an acid or base catalysed system, involves nucleophilic attack of the oxygen contained in water on the silicon atom. This has been confirmed by the
reaction of isotopically labelled water with TEOS where unlabelled ethanol was produced.[9] The reaction is shown in (2)

$$(OR)_3Si - OR + H^{18}OH \rightleftharpoons (OR)_3Si^{18}OH + ROH \quad (2)$$

The acid catalysed hydrolysis of TEOS is described in Scheme 1.1.

Scheme 1.1: Nucleophilic attack on the silicon atom in acid catalysed hydrolysis[10]

At low pH, the alkoxide group is protonated and this reduces the electron density at the silicon atom. The reduced electron density facilitates nucleophilic attack of the silicon atom by the oxygen atom in a water molecule. The alkoxy group is released and the silanol group is formed. The pentacordinate intermediate proposed in this scheme is consistent with the observation that tetralkoxysilanes with sterically bulky alkyl groups exhibit lower rates of hydrolysis.[9]

The base catalysed hydrolysis of TEOS is shown in Scheme 1.2.

Scheme 1.2: Base catalysed hydrolysis mechanism.[10]

The reaction is initiated by a nucleophilic attack at the Si atom by a hydroxyl ion. A pentacordinate intermediate facilitates the formation of the silanol and the release of an
alkyloxonium ion. The intermediate here suggests that rate of the base catalysed
hydrolysis is also subject to steric effects.

In both acid and base catalysed hydrolysis, inductive effects on the rate of reaction
result from the contribution of substituents on the silicon atom. This is important when
considering the effect of organic substituents other than alkoxy groups bonded to the
silicon atom (such as those present in organically modified alkoxysilanes) and the effect
they have on hydrolysis rate. A useful graphic developed by Brinker is shown in Figure
1.3.

Figure 1.3: Inductive effect of substituents bonded to the silicon atom. It must be noted
that the acidity and basicity referred to here is Lewis acidity and basicity. [9]

The inductive effect has a number of significant consequences. As the intermediates in
the case of acid and base catalysed hydrolysis differ in charge, the subsequent reactions
after the initial formation of a silanol group differ.

Silanol and siloxane substituents are both electron withdrawing groups and therefore
stabilise the negatively charged intermediate in the case of base catalysed hydrolysis.
Therefore a TEOS molecule that has formed one silanol group will react with hydroxyl
groups (according to Scheme 1.2) in its vicinity more readily as the intermediate is easier to form. This results in complete hydrolysis of the alkoxy silane under base catalysed conditions and consequently, the formation of denser networks of silica.

Conversely, the rate of subsequent hydrolysis reactions for a TEOS molecule containing one silanol group in acid catalysed conditions are reduced due to the inductive effect of the newly formed silanol group on the intermediate. Hydrolysis is not complete under acid catalysed conditions and it is assumed that condensation of the partially hydrolysed presursors proceeds. This effect results in the preferential formation of strand like oligomers as the acid catalysed system condenses and the effect of this is to produce porous silica condensates.

1.6.2 Solvent Effect

The co-solvent used will affect the rate of hydrolysis. Aprotic solvents will increase the nucleophilicity of hydrolysis initiating ions in solution. This is believed to be a result of their inability to hydrogen bond with ions therefore increasing their activity in the hydrolysis reaction. Alcohol based solvents can become involved in re-esterification reactions with the alkoxy silane during hydrolysis. As outlined in equation (1), the hydrolysis equilibrium will also be subject to the concentration of both the water and alcohol in the reaction mixture.[11]

1.6.3 Condensation

Silanols species in solution react with one another and form siloxane bonds through two different routes of condensation.

\[
(OH)_3 Si - OH + OH - Si(OH)_3 \rightleftharpoons (OR)_3 Si - O - Si(OH)_3 + H_2O \quad (3)
\]

\[
(OH)_3 Si - OR + OH - Si(OH)_3 \rightleftharpoons (OR)_3 Si - O - Si(OH)_3 + ROH \quad (4)
\]
The first produces water upon formation of the siloxane bond and the second produces alcohol. The initial dimer will react with silanols or other oligomers in solution and subsequently polymerise to form the trimer, the tetramer and so on, increasing the size of the condensate as it transitions from oligomer to polymer.[9] The nature of the polymerization, i.e. whether the polymer adopts chain-like structures or dense particles, will depend on the hydrolysis mechanism. The process may be considered to be a range of different condensation reactions happening simultaneously between a variety of possible starting compounds. Figure 1.4 demonstrates the range of monomers that may interact with each other during condensation of a simple alkoxyisilane such as TEOS.

![Figure 1.4: Schematic outlining possible reactants involved in the condensation of TEOS.][9]

While Figure 1.4 demonstrates the complexity of the reactants present during the condensation reactions, other important reaction variables such as the ratio of water to alcohol and the pH must be considered. The situation becomes more complex again when the nature of the organic moiety in a given ACA has to be considered. Depending
on the organic moiety, the reaction environment may be affected (as in the case of pH altering substituents) and also the rates of hydrolysis and condensation will depend on the electron donating or withdrawing nature of the substituent.[12]

Figure 1.5: The impact of acid catalysis on the structural properties on the resulting gel[10]

Figure 1.5 shows the impact of the use of acid catalysis when preparing a sol-gel. The linear structure of the oligomers and limited crosslinking can be seen. Figure 1.6 shows the impact of base catalysis on the sol-gel formation and structure.

Figure 1.6: The impact of base catalysis on the structural properties of the resulting gel[10]

A common feature of the final material produced by both systems is porosity. This porosity comes about by two different pathways. In the case of the acid catalysed sol-
gel the limited branching and preference for the formation of linear and cyclic oligomers produces nanometer scale pores throughout the sol-gel matrix. The base catalysed sol-gel is comprised of oligomers that condense thoroughly and form dense particles as the reaction proceeds. When the gel forms, the particles link together and the spaces between the particles are the pores.[13]

1.6.4 Hydrolysis & Condensation: Surface Modification / Sol-gel Formation

The aspects of hydrolysis and condensation of organofunctional alkoxysilanes are more clearly understood when they are placed in context. From the surface modification viewpoint it would appear that the acid catalysed approach will lead to more stable silanol functionalised coupling agents in aqueous solution. Fast, partial hydrolysis and slow condensation reactions are characteristics of this process.[13] It is also convenient that the organofunctional moiety on a given ACA will assist in retarding the rate of hydrolysis and aid in stabilising the silanol. This depends on the organic moiety on the ACA however. For instance, amine containing organic moieties will act as bases in aqueous solution and will facilitate the rapid formation of trisilanol products (in the case of trialkoxysilane ACAs) and also the subsequent condensation reactions.[12]

From the sol-gel science viewpoint, the desired physical characteristics of the material being produced will dictate the choice of reaction conditions. Acid catalysed hydrolysis will yield silanols that tend to form polymer chains during condensation. This leads to the creation of large networks of interconnecting siloxane strands. Base catalysed hydrolysis favours the total hydrolysis of the precursor. This results in compact particulate structures forming as the siloxane polymer forms. In the case of the latter, the well-known Stober synthesis method producing monodisperse spherical particles of silica with sizes ranging from 0.05 to 2µm was based on the study of silica produced using ammonia as catalyst in alcohol-water mixtures [14].
1.6.5 GM as an Alkoxysilane Coupling Agent

Having outlined the principles and theory of alkoxysilane chemistry for the viewpoint of both surface modification and sol-gel science, it is necessary to comment on where the GM fits into these overlapping disciplines. The obvious answer is the field of surface modification however the GM is incorporated in the rubber-to-metal adhesive formulation unhydrolysed and also, it is not administered using the traditional aqueous techniques that distinguish surface modification. It is applied with the intent of achieving the same goal but through a different method. It is assumed that the GM is not intended to form any kind of polymer matrix typical of the ormosils in sol-gel science. However, the application environment is challenging, featuring exposure to high temperatures as well as ambient humidity and atmosphere. In these circumstances the stability of the alkoxysilane moiety may not be guaranteed and hydrolysis/condensation may occur.

1.7 Natural Rubber

Natural rubber is a polymer consisting of a trialkyl alkene repeating unit which is in the cis formation.

![Figure 1.7: The structural unit of cis-1,4-polyisoprene, natural rubber.](image)

The cis structure of the polymer unit contributes to its elasticity. The trans isomer, gutta percha, is a hard material without any of the elastic properties of rubber [15]. The elasticity of NR results from the coiled polymeric strands uncoiling during stretching. While stretched, the polymeric strands align and become crystalline. The industrial
application of NR relies on the process of vulcanisation, developed by Charles Goodyear [16]. NR is thermoplastic in the absence of vulcanisation and loses its pliability and elasticity to become a hard brittle material at low temperatures. By mixing NR with elemental sulphur and heating the mixture, the polymer chains may be cross-linked (Figure 1.8). Vulcanization confers toughness and temperature stability while preserving elasticity. The vulcanization process can be controlled by varying the concentration of the sulphur and the curing time so that rubber materials with application specific physical properties can be produced.

![Diagram of natural rubber and vulcanisation process](image)

Figure 1.8: (a) Natural rubber exists as a long chain polymer, (b) vulcanisation, the reaction of NR with elemental sulphur cross-links the NR with sulphur based bridges. (c) The cross-linking prevents the unravelling of the NR polymer chains when the material is under stress, thereby enhancing its tensile strength.[15]

Given that NR is a polyene, it is vulnerable to attack by a wide range of electrophilic compounds. In order to extend the lifetime of the vulcanizate, antidegradants and antiozonants are incorporated in the unvulcanized blend. Vulcanizates of unsaturated
fats such as rapeseed oil (factices) may be included as diluents. Particulate fillers such as silica, titania, clay and carbon black are incorporated for rubber products that are subject to wear and tear e.g. car and truck tyres. In general, any unvulcanised rubber raw material contains an array of additives, the selection of which is determined by the end use of the vulcanizate.[8]

1.8 Nitroso chemistry of the Henkel Green Molecule

In order for the green molecule to be applied as a bridging molecule for the binding of natural rubber (NR) to inorganic substrates, it must contain an appropriate organic functional group that will bond covalently with the rubber. This role is performed by the nitroso functional group included in the design of the GM. The published research of nitroso compounds is rich and varied. Depending on the substrate to which they are bonded, the nitroso compound may undergo dimerisation at the functional group[17], [18]. In NMR spectroscopy, the in-plane ‘flipping’ of the nitroso group in nitrosoarenes results in an exchange process that has been the subject of several publications [19–21]. In coordination chemistry, the distribution of lone pairs of electrons at both the nitrogen and oxygen atoms results in a variety of coordination bonds that may be formed between a given nitroso compound and a transition metal ion [22], [23].

These are three examples of the many research areas relating to nitroso chemistry. In the context of this project, the most important aspect of nitroso chemistry is the reactivity of nitroso compounds with ene substrates.

1.8.1 Nitroso Compounds as Enophiles

The ene reaction is an indirect substitutive addition. The reactants are comprised of an alkene possessing an α methylinic hydrogen atom and a compound containing a double bond. These are referred to as the ene and the enophile respectively. There is a range of
reaction mechanisms that have been identified for ene reactions however concerted reaction and reaction via a biradical intermediate are common.

Scheme 1.3: Concerted ene reaction: general mechanism. [24]

Scheme 1.4: Ene reaction via biradical mechanism. [24]

Given the influence of the substrate to which the nitroso group is attached upon the products that result from a nitroso reaction, it is useful to classify the nitroso chemistry of the GM by relating it to nitroso compounds of similar chemical composition that have been analysed in the literature as enophiles. The reactivity of the organic moiety of the GM that has been incorporated to act as the nitroso enophile may be compared to that of N, N-dimethyl-4-nitrosoaniline (pDMNA). This is an electron rich enophile, comparable to p-nitrosophenol (pNP) and both compounds exhibit similar behaviour when reacted with ene substrates. The reactions are outlined in Scheme 1.5, Scheme 1.6 & Scheme 1.7. [25–27]
Scheme 1.5: The initial product from the reaction of an electron rich aryl nitroso enophile and an ene substrate is the aryl hydroxylamine.

Scheme 1.6: The hydroxylamine may undergo dehydration to form the imine.

Scheme 1.7: Thermal decomposition transforms the hydroxylamine into an N-alkenyl arylamine and also produces a nitrone.

It is appropriate here to omit the information relating to the products of the reaction of ene substrates and aryl nitroso compounds that are unsubstituted or substituted with electron withdrawing groups as this information is outside the scope of the project.
However if the reader is interested in the chemistry of these reactions, they are included in the references [25–27]. The initial product formed from the reaction of electron rich nitroso enophiles is the aryl hydroxylamine. Dehydration is likely, however evidence for it has not been reported. The product resulting from dehydration is the imine in Scheme 1.6. Thermal decomposition will result in the N-alkenyl aryl amine and the nitrone shown in Scheme 1.7. For the latter product, isolation and identification has not been achieved. This has been attributed to addition and cyclization reactions between molecules of the nitrone product.

1.8.2 Nitroso Compounds and Natural Rubber

The ene reactivity of nitroso compounds has been applied in the modification and crosslinking of NR. In the earliest report regarding interactions between nitroso compounds and NR, Pummerer and Gundel indicated that nitrosobenzene reacted with isoprene rubber at a ratio of 3 nitrosobenzene molecules for every one isoprene site on the polymer chain. The reaction yielded what was described as ‘an isorubber nitrone’ product as well as azoxybenzene and phenylhydroxylamine as side products.[28]
X may indicate NH$_2$, NHR, NR$_2$ or OH.

Baker et al investigated the use aryl nitroso compounds $p$-nitrosophenol and $p$-nitroso-
dimethylaniline as additives to NR blends in order to facilitate crosslinking with the
addition of an agent such as a diisocyanate compound. The strategy employed involved
grafting the aryl nitroso compound to the NR polymer backbone, the $para$ substituent of
the compound then being available for crosslinking. It was reported that the most
satisfactory system developed during the course of the study involved the initial
reaction of $p$-nitrosophenol with a diisocyanate to form a novel nitroso functionalised
diurethane that was then added to the NR blend. This strategy was preferred as it
avoided working with the nitroso compounds directly, as they are responsible for severe
staining. In this report, the ene reaction of the electron rich aryl nitroso compound is
outlined. The reaction as reported is shown in Scheme 1.8. [29]
Figure 1.9: A schematic of the covalent bonding of NR antioxidants to the polymer chain using secondary amine linkage. The covalent link is formed by the ene reaction of the aryl nitroso with NR [30].

Cain *et al* investigated the use of 4-nitrosodiphenylamine (NDPA) as a covalently bonded antioxidant in NR. The performance of the nitroso based antidegradants was compared with *p*-phenylenediamines with the former exhibiting resistance to extraction by solvents or other methods from the cured rubber. In this report, the formation of nitrones resulting from the ene reaction of the nitroso compound and the isoprene unit of the rubber polymer was addressed and reported as being produced in equal yield to that of the *p*-phenylenediamine.[30]

Kavun and Federova investigated the reaction of NDPA with NR also. They reported the isolation of N-phenyl-*p*-phenylenediamine side products from the NR-NDPA blend. Furthermore, the viscosity of the NR was seen to decrease with the addition of NDPA. This was interpreted as indicating a reaction between the NDPA and NR that involves scission of the polymer chain. In this report, the formation of radicals at both the ene and enophile are the driving force for the reaction and the ene mechanism proposed by the authors mentioned above is not discussed. [31]
Kogan et al. reported similar findings to those of Kavun and Federova while investigating the reaction of $N, N$-diethyl-4-nitrosoaniline (DENA) and cis-1,4-polyisoprene (C-1,4-PI). A mechanism was proposed for the reaction of the DENA that included an initial dimerization step involving two molecules of DENA. This dimer does not appear to be similar to the kind of dimerization that is typical of many but not all aryl nitroso compounds. The dimer subsequently forms a tetrahydra oxadiazole ring in conjunction with the double bond on the natural rubber backbone which subsequently breaks. In this way, the authors have proposed an explanation for the chain scission that was observed. [32]

1.9 Steel Substrates in Rubber-to-Metal Bonding

Many assemblies that incorporate rubber-to-metal bonding in their design use low carbon steels that possess strength and ductility. Low carbon steel is susceptible to corrosion and requires protection from atmospheric and environmental corrosion. A range of methods is available for protecting the surface of the steel component once it has been produced. These include hot dip galvanizing, painting, packaging the metal in paper impregnated with VPIs (vapour phase inhibitors) and chemical conversion coatings. A conversion coating may perform as a barrier between the substrate and corrosive materials in its environment. There are also conversion coatings that protect the substrate in an active manner, releasing active chemical species at sites where the conditions for corrosion have become established. There is a range of conversion coatings, each with their own chemical composition.[33]

Chromate conversion coatings offer excellent corrosion protection as well as compatibility with organic coatings should they require application to the piece. They have been shown to be self-healing. The self-healing action arises from mobile
chromate ions in the body of the conversion coating that migrate to sites in the coating where the substrate has been exposed through damage.[34] At the exposed site the chromate (VI) ions precipitate and form a fresh Cr (III) coating layer protecting the substrate. However chromate ions are harmful to the environment and are also known carcinogens. Therefore their use is being phased out and safer alternatives are sought.[35]

Iron phosphate conversion coatings are deposited from baths containing alkali phosphates. The coating weight is low (ca. 0.3-0.9 gm\(^{-2}\)) and the coating is amorphous. It is comprised of a mixture of vivianite (Fe\(_3\)(PO\(_4\)).8H\(_2\)O) and γ-Fe\(_2\)O\(_3\) with about 35% of the former making up the coating. The process is environmentally friendly given that the solution from coating baths and spray processes are easily remediated before disposal. [36]

Zinc phosphate conversion coatings (ZPCCs) are the most widely applied corrosion protection for steels. The quality of the conversion coating is highly dependent on the process conditions and the surface preparation of the substrate. Variable process conditions include the composition of the phosphating solution as well as its pH and temperature. Mechanical and electrochemical acceleration may also be used. The coatings may be applied by immersion or spraying, each method producing coatings with different physical characteristics. [37]
ZPCCs consist of two phases of crystal structure. At the substrate-coating interface, phosphophyllite is formed which incorporates Fe from the surface and has the chemical composition FeZn₂(PO₄)₂·4H₂O. The phosphophyllite precipitates during the initial stages of the coating process and is followed by the growth of the bulk of the coating which consists of hopeite (Zn₃(PO₄)₂·4H₂O). [38] Low zinc phosphating baths have been used in order to encourage the formation of phosphophyllite which has better stability at high temperature and high pH.[35] In general, ZPCCs are porous and may require some post treatment to ensure complete protection.[33] They are also stable at pH 3-12. The water of crystallization of the coating may be lost during heating with the hopeite rehydrating upon cooling while the phosphophyllite does not.[39]
1.10 Research Objectives

The GM is a complex alkoxysilane coupling agent that is applied as part of a formulation in its unhydrolysed state. The application environment in the context of this project is an injection moulding process. Prior to application of NR to the metal or coated metal substrate, the part is subject to a prebake step. This lasts for 5 minutes and the temperature for this step is 160 °C. It is expected that such a thermal stress will cause chemical changes to occur in the alkoxysilane coupling agent. Substrates of interest include mild steel and zinc phosphate coated mild steel. Therefore the following research objectives have been identified:

- To identify any intramolecular or intermolecular changes induced in the GM by thermal stress. (Ch. 4)
  - This chapter will present findings from the investigation of the general thermal stability of the GM without taking into account for direct interaction with either the rubber or metal.

- To investigate how the GM interacts with a mild steel substrate. (Ch.5)
  - The chemical interaction of the GM with a mild steel substrate is investigated in the context of the prebake step outlined in section 1.4.

- To investigate the chemical stability of more complex substrates (e.g. zinc phosphate coated mild steel) in the application environment. (Ch.5)

- To investigate the reactivity of the nitroso moiety of the GM with the primary component of the NR, the cis-1, 4-polyisoprene. (Ch. 6)
  - The results of solution NMR studies and experiments carried out between the GM and NR in the injection moulding process are presented.
To examine the effect of thermal stress on the rubber-to-metal formulation containing the GM. (Ch. 7)

- The effect of thermal stress on adhesion samples prepared using the injection moulding process and employing the GM in the commercial adhesive formation are presented.
1.11 References


bound and related Novel Antioxidants, Rubber Chem. Technol. 45 (1972) 204–221.


2 Chapter 2: Analytical Techniques

2.1 Introduction

The analytical techniques that were used during the course of the project are presented in this chapter. Where necessary, the underlying theory that underpins the principle operation of a given technique has been presented.

2.2 Theory of Vibrational Spectroscopy

The atoms that comprise a given molecule vibrate about their equilibrium positions. This vibrational motion may be modelled using the classical analogy of the simple harmonic oscillator. The oscillation frequency, potential and total energy of a mass on a spring (an example of a one dimensional harmonic oscillator) are expressed, using classical mechanics, by the following equations:

\[ \omega = \frac{k}{\sqrt{m}} \]  

(1)

\[ U = \frac{1}{2} k x^2 \]  

(2)

\[ E = \frac{1}{2} k x_m^2 \]  

(3)

\( \omega \) is the angular frequency in radians, \( k \) is the spring constant and \( m \) is the mass. \( x \) is the displacement and \( x_m \) is the maximum displacement. The energy of the system varies continuously with displacement. The frequency is a function of the spring constant and the mass. To apply this model at the atomic scale, the Schrödinger equation for the simple harmonic oscillator must be prepared.

\[ -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2} k x^2 \psi = E \psi \]  

(4)
Solutions to this equation differ from those of the classical oscillator in a number of important ways. The energy of the oscillator is not continuous. There are allowed energy levels that are separated by equal amounts of energy.

\[ E_n = \left( n + \frac{1}{2} \right) \hbar \omega_0 \]  

(5)

The energy at the ground state \( n = 0 \) cannot be zero. This is a result of the uncertainty principle. If the ground state energy was zero, both the position and momentum of the particles being modelled would be known. A further consequence of the quantum mechanical treatment of the simple harmonic oscillator requires that transitions between vibrational states are subject to the following selection rule.

\[ \Delta N = \pm 1 \]  

(6)

The application of the quantum mechanical analysis of the simple harmonic oscillator for multi atom molecules is more complex but general aspects of the one dimensional analysis hold. The most important aspects of the results of the quantum mechanical treatment as follows:

- Chemically bonded atoms absorb and emit infrared electromagnetic radiation in discrete quantities
- The quantity of energy of the electromagnetic radiation depends on the mass of the atoms, the electronegativity of the elements and the type of bond

These features of the mechanism of interaction of electromagnetic radiation and molecules allow for the analysis of the molecular structure by examining the absorption fingerprint it possesses. For instance, changes in the bonding can be detected as well as changes in intermolecular reactions such as hydrogen bonding and dipole-dipole
interactions by recording the spectra of the compound under some environmental stress such as increased temperature. [1]

2.3 Raman Spectroscopy

Raman spectroscopy is a tool for analysing the molecular structure of inorganic and organic compounds. The sample under analysis is subjected to monochromatic light. The photons from the light source collide with molecules in the sample and these collisions may be elastic or inelastic i.e. energy is conserved, lost or gained by the photon through the collision. The amount of energy lost or gained is determined by the energy of the vibrational states of the molecule. The light reflected or scattered from the sample is directed through a diffraction grating to a detector to determine the wavelength change. In this manner the energy gained or lost during its interaction with the compound can be determined. If energy has been lost the shift is referred to as a Stokes shift and if energy has been gained, it is referred to as an anti-Stokes shift.[2]

The anti-Stokes shifts are weakly detected as they are a result of photons interacting with thermally excited vibrational states which are a small percentage of those occupied by the molecule. Therefore Raman spectroscopy is concerned with the more easily detected Stokes shifts. The energy loss of the photon will be characteristic of a given vibrational state of molecule and this yields very useful information on the composition of the compound.

Raman spectroscopy is a complementary technique to infrared spectroscopy i.e. Raman spectroscopy can reveal information about the vibrational states of a molecule that may not be revealed by infrared spectroscopy and *vice versa*. The symmetry point group of the molecule will determine whether or not the vibrational states it occupies will be Raman or IR active. In general, point groups with higher symmetry such as the
tetrahedral point group will possess fewer IR and Raman peaks due to degeneracy and few of these will be both Raman and IR active. The vibrations will tend to be either Raman or Infrared active. Molecules of lower symmetry will possess more vibrations that will appear in both IR and Raman spectra.[3]

This is a very simplistic outline of the principle of operation of Raman spectroscopy and more thorough reviews of the theory of Raman scattering are available. [4], [5]
Figure 2-1: Schematic of the coupling of the Raman detector and the microscope. [6]

Pictured right is a Jablonski diagram outlining the Raman effect. [2]

2.4 External Reflectance Infrared Spectroscopy

Infrared spectroscopy, as outlined above, is a complimentary technique to Raman spectroscopy.

Whereas Raman spectroscopy is a scattering phenomenon, Infrared spectroscopy relies on the absorption of far (200-10cm\(^{-1}\)), mid (200-4000cm\(^{-1}\)) or near (12500-400cm\(^{-1}\)) infrared radiation. In general, the mid IR region is that which is most frequently analysed. The frequency of the absorbed radiation yields information on the kind of vibration within the molecule that has been excited. The frequency of the vibrations that may be detected for a given molecule is dependent on the bond type and the atoms involved in the bond. Therefore, IR spectroscopy can be used to determine the chemical
composition of a compound. A requirement of IR spectroscopy is that there must be a change in the dipole moment of the bond associated with the vibration in order for it to be detected. [7]

External reflectance spectroscopy may be used for the analysis of thin films on reflective surfaces.[8]

A microscope is coupled to the IR spectrometer, parfocal with the path of the IR radiation that will be used to analyse the sample. Conventional glass optical lenses are opaque to IR radiation and are replaced with Cassegrain reflecting optics. This combination of microscope optics and spectroscopy has many advantages. Sample surfaces may be analysed with little or no preparation, and it is non-destructive. Mapping is possible whereby an area of a surface may be reproduced with a ‘false colour’ overlay that tracks the presence of different compounds in a sample. There are disadvantages associated with reflectance spectroscopy. Optical phenomena may distort the IR spectrum of the sample however these effects can be accounted for and corrected.[9]
Figure 2-2: A schematic of the external reflectance infrared microscope.[9] The instrument used in this project is pictured on the right

### 2.5 Attenuated Total Reflectance Infrared Spectroscopy

ATR infrared spectroscopy is another example of the coupling of a special optical accessory to an infrared spectrometer. It is useful for producing IR spectra of solid or liquid samples. The sample is placed in direct contact with the face of an internal reflection element (IRE). The IRE is a crystalline material that is transparent in the IR region of the electromagnetic spectrum. Zinc selenide and thallium bromide crystals may be used however, diamond IREs are popular as they are strong enough to withstand the pressure that may be applied when achieving satisfactory contact between the IRE and the analyte. IR radiation is incident on the IRE at an angle less than that required for total internal reflection. This causes the IR beam to be reflected repeatedly within the crystal before being directed back to the detector. At each point of reflection the IR beam produces an evanescent wave which penetrates into the sample in contact with the surface. In this way, absorption of the IR radiation occurs and a spectrum of the sample is produced. The penetration depth of the evanescent wave is approximately 1µm however this is wavelength dependent.
\[ d_p = \frac{\lambda_1}{2\pi n_1 (\sin \theta^2 - n_{21}^2)} \]  
(7)

Where \( d_p \) is the penetration depth, \( n_1 \) is the index of refraction of the IRE, \( n_2 \) is that of the sample, \( n_{21} \) is the ratio of the indices of refraction and \( \lambda_1 = \lambda_{\text{vacuum}}/n \). The ratio of the peak heights of the spectrum of a given analyte will differ from those in the spectrum recorded using conventional transmission optics. This can be corrected easily using the software provided with the spectrometer.[10]

Figure 2-3: The ATR crystal and the path of the infrared radiation.[10] The instrument used in this project is pictured on the right.

### 2.6 Atomic Force Microscopy Infrared Spectroscopy (AFMIR)

As outlined in section 2.3, IR microscopy is very useful for determining the distribution of materials in a sample by way of mapping the absorption profile of the compounds of which it is comprised. This is a powerful tool however samples with dimensions that are smaller than the diffraction limit of the IR illumination may not be distinguished from the matrix. The recent combination of AFM and IR spectroscopy has overcome this limitation. The technique relies on the combination of tunable infrared lasers and an
AFM cantilever to detect localised vibration excitations with a very high resolution. The experimental set up is shown in Figure 2-4.

![Diagram of the Anasys AFMIR system](image)

Figure 2-4: (a) The Anasys AFMIR system. A tunable IR laser is used to excite molecular resonances in the sample. IR absorption at the sample induces rapid thermal expansion, exciting resonance oscillations at the cantilever. These 'ringdowns', (b) can be analysed using Fourier techniques (c) to measure the amplitude and frequency of oscillation. (d) The cantilever oscillation frequency plotted as a function of the IR source wavelength creates the local absorption spectrum.[11]

The sample is scanned in the usual manner using the AFM, cantilever mounted tip. Once the scan has been completed, the area of interest is identified and the tip is positioned at this site. The site is then illuminated by an Infrared laser source. Thermal expansion at the vibrational absorption frequencies of the material under interrogation is induced and detected by the AFM tip. The laser is pulsed so that a decaying signal is
produced and this may be analysed using Fourier transform to determine the component frequencies of absorption. In this manner, features with dimensions on the nanometre scale can be analysed and their vibrational spectra determined.\cite{12, 13} AFMIR analysis for this project was carried out by Anasys engineers at their facility in Santa Barbara. Unfortunately, AFMIR systems may still be considered to be in a developmental stage and the availability of access to such instruments at this time is limited.

2.7 Derivative Analysis of IR Spectra

Second derivative spectroscopy is a technique that allows for the simplification of absorption peaks that contain overlapping peaks. As shown in Figure 2-5, the even numbered derivatives of the zero order bands result in bands that have a smaller full width half maximum absorption (FWHM) or bandwidth. In the case of Lorentzian absorption bands, which are typical of IR spectra, the FWHM of the second derivative can fall to as much as one third of the FWHM of the original, zero order absorption bands. It is this reduction in bandwidth that improves the resolution of the treated spectrum and that may allow for the distinction of the bands that are overlapping in the zero order spectrum.
Figure 2-5: The effect of derivative spectroscopy on Gaussian (solid line) and Lorentzian (dashed line) absorption bands. (a) represents the zero order or undifferentiated peak. (b) to (e) show the effect of first to fourth order differentiation of the zero order band. [2]

2.8 X-Ray Photoelectron Spectroscopy (XPS)

XPS is a useful analytical tool for probing the elements that comprise the surface of a substrate and also the oxidation state in which they are found. The fundamental process underlying XPS is the photoionization of the analyte and the subsequent analysis of the energy of the expelled electron. An X-ray ionization source is used to expel inner shell electrons from the sample which are then collected by an electron beam analyser and sent to a detector. The kinetic energy of the expelled electron is the difference between the incident photon and the binding energy of the electron. The photoelectrons are typically expelled from the first 2-10 nm of the samples surface. The binding energy of the photoelectron can yield information regarding the oxidation state, organic structure
and bonding environment of the detected element. XPS analysis allows for accurate differentiation of elements at the surface and is sensitive to all elements with \( Z > 2 \). [14–16]

![Diagram including the XPS (here labelled the ESCA) process][14]

Figure 2-6: Diagram including the XPS (here labelled the ESCA) process[14]

The XPS analysis for this project was carried out by Dr Steve Hinder of the University of Surrey.

### 2.9 Scanning Electron Microscopy (SEM)

SEM is an advanced microscopic technique that allows the user to record images in which sample features with dimensions in the nanometer scale may be clearly distinguished. The design of the SEM follows the traditional design of optical microscopes in that an illumination source, a condenser lens and an objective lens are all present. The distinguishing feature is that whereas an optical microscope relies on visible light to illuminate and form a magnified image of the sample, SEM uses a beam of electrons to perform this task. Therefore the refractive glass objective and condenser lenses of the optical microscope are replaced using magnetic equivalents. These focus and control the beam using magnetic fields which exert a force on moving electrons.
Another difference between optical and electron microscopy is that the particles comprising the electron beam are negatively charged and this must be compensated for, again through the application of magnetic fields. A stigmator is used in this instance to provide an electron beam that is homogeneous.

The beam is raster scanned on the sample surface as the name of the technique implies. Electrons incident on the surface may, depending on their energy produce a variety of signals from the sample surface. These signals include (i) secondary electrons, (ii) backscattered electrons and (iii) x-ray photons.

### 2.9.1 Secondary Electrons

Secondary electrons: the sample may be ionised by the incident electron beam and the electrons released when ionisation occurs are described as secondary electrons. The signal associated with secondary electrons originates at the surface and because of this, images recorded using the secondary electron signal produce very high resolution images. This signal contains no information regarding the elemental composition of the sample in contrast to the backscattered electron signal. It is also extremely sensitive to charging which occurs in insulating samples and causes deterioration of the quality of the image.
Figure 2-7: An image recorded using the CREST Hitachi SU-70 FESEM. The secondary electron detector is used here to image silica coated Fe microparticles. Charging resulting from the non-conducting surface is readily observed in this image.

2.9.2 Backscattered Electrons

Backscattered electrons: as the name suggests these electrons are scattered from the incident beam by the sample. The interaction is influenced by the atomic number of the element involved and this results in an increasing intensity of the backscattered electron signal as the atomic number of the interacting element increases. In practice, the brighter the region or feature on the backscattered electron image, the higher the atomic weight of the elements present in that region or feature. This can be useful for making rapid, qualitative observations on the elemental composition of a given sample. Unlike, secondary electrons, backscattered electrons are not surface specific and can be generated from below the surface of the sample. This reduces the resolution of the image produced by backscattered electrons.
Figure 2-8: The same image in Figure 2-7 recorded using the backscattered electron detector.

2.9.3 X-Ray Photons

X-ray emission occurs in a sample when the incident electron ejects an inner shell electron. The process whereby an outer shell electron occupies the vacancy left by the ejected electron results in the emission of an X-ray. The energy of the X-ray is specific to the element in question and by collecting and determining the wavelength of X-rays emitted by the sample; the elemental composition can be elucidated. In modern instruments, elemental maps can be prepared of the surface. These indicate clearly the distribution of elements in the area being analysed.[16]
Figure 2-9: Electron image of a painted metal substrate cross section. EDX mapping shows the elemental composition of a paint layer (d), a primer layer (c) and an electrodeposited metal layer on a metal substrate (b).

2.9.4 Sample Preparation

Sample composition and preparation are important factors to be considered when preparing to perform SEM imaging or energy dispersive elemental analysis (EDX) of a sample. Non conducting samples may be coated using noble metals or Carbon through sputtering or evaporation techniques respectively. The sample cannot contain moisture or sources of outgassing as this will degrade the vacuum in the column. This will interfere with the electron beam and results in poor quality imaging or analysis.[17]
2.10 Energy Dispersive X-Ray Analysis (EDX)

As outlined above in section 2.8, X-ray photons released from the sample by the incident electron beam may be used to perform elemental analysis on a given sample surface. Typically, the energy of the incident electron beam will need to possess twice the energy in eV of the X-ray that is to be detected. X-ray analysis generally requires high accelerating voltages for the electron beam and this increases the interaction volume of the beam with the sample. Therefore it is best practice to use the backscattered electron detector, which shows an image faithful to the penetration depth of the electron beam, in tandem with the EDX detector when performing analysis. Modern instruments allow for a variety of methods of analysing the surface including point, line and mapping analysis. Mapping analysis is very useful as a false colour image can be prepared that indicates the areas on a surface in which a given element is present. For example, painted substrates that may have a number of different coats can be analysed and the constituent elements of each coat distinguished clearly in the elemental map.
As a qualitative tool, EDX is very useful as it clearly indicates whether or not an element is present in the region of interest. Care must be taken to ensure that misinterpretation of the analysis is avoided however as some X-ray emission lines may overlap for some elements. Double counts from strong signals (i.e. elements with high concentration in the matrix) are also sources of error and must be taken into account for.

Quantitative analysis is difficult to achieve with a given EDX workstation as it is required that the sample be as close to perfectly flat as possible. Any significant surface roughness will introduce error into the quantitative analysis being undertaken. This limits the amount of practical samples that can be analysed in this way using the EDX detector system and its software.[18]

2.11 Thermogravimetric Analysis and Differential Thermal Analysis

Thermogravimetric analysis refers to the recording the mass of analyte as a function of temperature. This is useful for tracking the loss of mass that occurs in a sample as it breaks down. Differential thermal analysis (DTA) is usually recorded in tandem with the thermogravimetric characteristics of the sample. Using DTA the energy required to heat a sample at the same rate as a thermally inert reference is recorded. The change in energy required as a function of temperature may then be used to identify thermal events in the sample that occur without any mass loss. Exothermic and endothermic events can be identified and these may than be interpreted given the sample type and the thermal behaviour that is expected to be observed.[19]
2.12 Nuclear magnetic Resonance Spectroscopy

NMR spectroscopy is a powerful analytical technique used for structure elucidation in chemistry. The general outline of the technique will be presented in these sections. It will begin with a general outline of the theory and execution of simple proton NMR experiments including the 90° pulse acquire experiment and the spin echo experiment. This will be followed by the INEPT (insensitive nuclei enhanced by polarization transfer) experiment used for the elucidation of the chemical environments of weakly detectable nuclei. The vector model will be used to outline the techniques already mentioned. Following this, product operator formalism will be used to more rigorously present the theory underpinning these experiments.

2.12.1 Spin

Spin is a property of subatomic particles such as protons and electrons that plays a crucial role in the manner in which these particles interact with each other and with electromagnetic radiation. A complete presentation of spin is outside the scope of this section but those aspects that are significant in the context of NMR will be presented.

Figure 2-11: A schematic of the signal path of a typical TGA/DTA.[19] The instrument used in this project is pictured on the right and simultaneously performs TGA and DTA on a given sample.
Spin refers to an intrinsic angular momentum possessed by subatomic particles. The magnetic moment of a given particle is a consequence of spin and it is this physical property that is of principle interest when discussing NMR spectroscopy. Nuclei may be categorised by the spin they possess.

<table>
<thead>
<tr>
<th>Nucleus Spin</th>
<th>I</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>0</td>
<td>$^{12}$C, $^{16}$O</td>
</tr>
<tr>
<td>½ Integer</td>
<td>$\frac{1}{2}$</td>
<td>$^{1}$H, $^{13}$C, $^{15}$N, $^{29}$Si</td>
</tr>
<tr>
<td>Quadrupolar ½ integer</td>
<td>$\frac{3}{2}, \frac{5}{2}, \frac{7}{2} \ldots$</td>
<td>$^{37}$Cl, $^{23}$Na</td>
</tr>
<tr>
<td>Quadrupolar Integer</td>
<td>1, 3, 4, 5 \ldots</td>
<td>$^{14}$N, $^{2}$H</td>
</tr>
</tbody>
</table>

Table 2-1: Nomenclature and examples of nuclei possessing different spin[20]

Zero spin nuclei are regarded as NMR silent as they have no interaction with an applied magnetic field. The following three categories are all affected by interaction with an applied magnetic field. The effect of a magnetic field on a nucleus possessing non-zero spin is to disturb the degeneracy of the ground state energy sublevels associated with the spin of the nucleus. The number of energy sublevels into which the ground state splits depends on the spin as follows: $(2I+1)$. For example, the ground state of a $\frac{1}{2}$ spin nucleus such as that of hydrogen or the $^{13}$C isotope will split into two sublevels. The $^{27}$Al isotope with spin 5/2 will split into six distinct sublevels.[20]

2.12.2 The Vector Model

Quantum mechanical treatments of the phenomena that underpin NMR spectroscopy are useful for determining the energy differences and degeneracies associated with nuclei. However, in order to present the processes that occur during simple NMR experiments, an alternative model is used: the vector model. The $\frac{1}{2}$ spin nucleus of the hydrogen atom is used here in order to present the vector model.
The hydrogen nuclei of a given analytical sample may be regarded as behaving as small bar magnets, the dipoles of which are orientated randomly. This is regardless of whether a magnetic field is present or not. When the sample is placed in a magnetic field there is a period of time that elapses before the sample comes into equilibrium with the field. This delay is expressed by the longitudinal relaxation time constant and it is subject to physical properties of the sample such as viscosity, composition and temperature. Once in equilibrium with the magnetic field, the magnetic moment of the sample can be described by a bulk magnetization vector. This may be regarded as a vector sum of the magnetic moments of the nuclei that have aligned with the field. It must be stressed that the number of nuclei that are aligned in this manner represent a small portion of the molecules that comprise the sample. The bulk magnetization is that which is represented by the magnetic moment in the vector model.[21]

Figure 2-12: The bulk magnetization vector of an NMR sensitive sample in an applied magnetic field $B_0$[22]

The vector model is based on this bulk magnetization vector and a right handed axis. The vector $M$ appears stationary however it will precess about the $z$ axis if it is tilted
toward the xy plane by a given angle. This precession has a specific frequency known as the Larmor frequency and depends on the gyromagnetic ratio of the nucleus in question and the applied magnetic field. In order to simplify the representation of the sample’s bulk magnetization, it is convenient to use a rotating frame of reference or axes. The set of axes are deemed to be rotating at the same frequency as the Larmor frequency of the nucleus and this eliminates any complications that arise when considering a precessing vector and its time dependent nature.[23]

To record the magnitude of the magnetization vector for a given sample, it is necessary for the vector to be orientated in the xy plane. In order to achieve this ‘flipping’, a magnetic field must be applied perpendicular to that of the applied field. This field must be strong enough to overcome the alignment induced by the applied magnetic field. This is achieved by using a short pulse of radio frequency radiation at a frequency equal to that of the Larmor frequency. The angle of the ‘flipping’ induced by the pulse is dependent on the applied field and the duration of the pulse. By matching the frequency with or close to that of the Larmor frequency of the nuclei of the sample, there is a resonance interaction between the radiation and the particle and this induces the necessary flipping.

![Diagram of flipping of the bulk magnetization vector](image)

Figure 2-13: Flipping of the bulk magnetization vector M by the radio frequency pulse [22]
Once the vector M has been ‘flipped’, the magnetization induces a signal in the detector and this is recorded as the free induction decay or FID signal. The decay is associated with the relaxation of the transverse magnetization as the vector M returns to the z axis.

Refocussing of the vector M associated with hydrogen nuclei in compounds that contain more than one hydrogen nuclei is often very useful. It is a multi-pulse experiment that allows for the elimination of phase errors caused by the offset of the nuclei with respect to the detector.

Figure 2-14: The spin echo experiment. The pulse sequence for the spin echo is given above the vector diagrams. [24]

Here the pulse sequence and its effect on the bulk magnetization vector in the xy plane is shown. At t=0 the vector M has been flipped onto the positive x-axis by a 90 ° pulse. After a delay τ the vector has precessed in the xy plane by an offset dependent angle. The 180 ° pulse applied after τ rotates the vector and its direction of precession around
the x axis back on to the xy plane. The vector is now allowed to precess for a second τ delay. After this delay, the vector M has been returned to the positive x axis. This is very useful when there are more than one magnetization vector representing a variety of hydrogen nuclei and precessing at different frequencies.

2.13 29Si Nuclear Magnetic Resonance (NMR) and Product Operator Formalism

The sensitivity of the silicon nucleus to FT NMR techniques is reduced (in comparison to nuclei such as hydrogen or fluorine) by the following factors.

Firstly, naturally occurring silicon is a mixture of three isotopes; 92.21% 28Si, 4.70% 29Si and 3.09% 30Si. Of these, 29Si is NMR active with a spin, I=1/2. Its abundance is low, comparable to that of 13C. [25]

Secondly, the gyromagnetic ratio of 29Si is negative and approximately one fifth of that of 1H (γ= - 5.3188 (107 radian T⁻¹ s⁻¹). The gyromagnetic ratio determines the energy difference between the high and low energy states of the NMR active nucleus in an externally applied field. The lower it is, the smaller this difference and hence the lower the sensitivity of the nucleus to detection. Also, the negative value of the gyromagnetic ratio is significant when taking into account Nuclear Overhauser effects (NOE). In the case of 13C, NOE can facilitate the enhancement of the insensitive nucleus detection; however, if γ is negative, the effect causes the signal to be reduced and may even result in null signal detection. [23]

Finally, the longitudinal magnetisation relaxation time T1 of silicon nuclei is long in comparison with that of 1H and 13C. This requires longer delays between pulse sequences in order to ensure full relaxation has taken place and as a result, slows down
the recording of multiple scans which are necessary to achieve a satisfactory signal to
noise ratio in the final spectrum.[26]

These factors make the detection of the $^{29}$Si nucleus in organosilicon compounds
significantly slower than that of $^1$H and $^{13}$C nuclei.

The sensitivity of $^{29}$Si NMR can be improved by applying multi-pulse experiments that
capitalise on polarization transfer from NMR sensitive nuclei located in the vicinity of
the silicon nucleus in the compound under examination. Insensitive nucleus
enhancement through polarization transfer (INEPT) is a technique that uses a
combination of pulses and delays to achieve polarization transfer. The following
discussion uses the vector model to present how the multi-pulse experiment achieves
this sensitivity enhancement.

It must be noted that product operator formalism may be used to present a more
rigorous model of the evolution of a given spin system during multi-pulse experiments.
The reader is directed to the following references. [27–29]
The vector diagram for the INEPT pulse sequence is much more complex than those already presented and it is worthwhile to spend some time to describe the initial state (a). Four vectors are shown on the rotating frame axis; these are $H_A$, $H_B$, $I_A$ and $I_B$. The necessity for the subscripts $A$ and $B$ arises from the difference in the number of sensitive nuclei ($H$) and insensitive nuclei ($I$) that contribute to the bulk vector magnetization in the sample. The proportion of spins in a sample placed in a magnetic
field that align in the direction of the field, thus adopting the lower energy sublevel induced by the field is given by the following equation:

\[
\frac{N_q}{N_p} = \exp\left(-\frac{\gamma \hbar B_0}{kT}\right)
\]

where \(N_q\) is the number of nuclei aligned with the external field, \(N_p\) is the total number of nuclei, \(\gamma\) is the gyromagnetic ratio, \(\hbar\) is Planck’s constant, \(B_0\) is the applied magnetic field, \(k\) is the Boltzmann constant and \(T\) is the temperature. The important term in this equation is the gyromagnetic ratio, \(\gamma\) which is of a larger magnitude for NMR sensitive nuclei than for insensitive nuclei. The consequence of this is that the population difference of the sensitive nuclei in the sample is always greater than that of the insensitive nuclei. The necessity to distinguish the magnetization vectors of I and H with the subscripts A and B in (a) reflects that there are insensitive spins coupled to the sensitive spins that contribute to the bulk magnetization vector and that these are not all aligned with the applied magnetic field. It is this population difference between the spin states of the sensitive and insensitive nuclei that underpins the INEPT population transfer experiment. [31]

The initial state of the coupled system is shown in (a) has been presented. A 90 ° pulse on the sensitive nucleus flips the \(H_a\) and \(H_b\) vectors on to the xy plane. (b) After a period \(\tau\) the H vectors have precessed in the xy plane by an equal amount but in opposite directions. The precession frequency in this instance is determined by the coupling (\(J\)) between the I and H nuclei. For the INEPT pulse sequence to deliver the optimum enhancement of the insensitive nucleus signal, the delay, \(\tau\) is set 1/4\(J\). (c) A 180 ° pulse is applied to both the I and H nuclei. The pulse on the H nucleus has the effect of flipping the H vectors to the opposite side of the xy plane. The pulse on the I
nucleus has the effect of altering the direction of precession of the H vectors. (d) The H vectors are allowed to precess for another delay of duration \( \tau \) until they are oppositely orientated on the xy plane. (e) 90° pulses applied to both the I and H result in the orientation of the vectors shown in (f) and (g).[30]

The overall result of the INEPT pulse sequence is to render insensitive nuclei that are undetectable under normal conditions, detectable by capitalising on the coupling between the insensitive and sensitive nuclei. At the end of the vector model in (a)-(g) we see that the \( I_a \) and \( I_b \) vectors are both in the xy plane and may be detected by the recording the free induction decay signal associated with their magnetization. The theoretical enhancement can be expressed using the following equation:

\[
E_d = n\left(\frac{\gamma_H}{\gamma_I}\right) \sin(\pi J \Delta) \cos^{n-1}(\pi J \Delta) \sin(2\pi J \tau)
\]

\( E_d \) represents the theoretical enhancement, \( n \) is the number of nuclei to which the insensitive nucleus I is coupled, \( \gamma_I \) and \( \gamma_H \) represent the gyromagnetic ratio of the insensitive and sensitive nucleus respectively, \( J \) is the coupling constant and \( \tau \) is the delay between pulses. \( \Delta \) is the delay between the final pulses shown in Figure 2-15. The magnitude of \( \Delta \) is at an optimum when:

\[
\Delta_{opt} = \left(\frac{1}{\pi J}\right) \sin^{-1} n^{-1/2}
\]
2.14 References


Chapter 3: The Effect of Thermal Stress on the GM Structure: 
Vibrational and Nuclear Magnetic Resonance Analysis

3.1 Introduction

The Henkel GM is applied as part of a rubber to metal adhesive formulation. Apart from an indication of the kinds of solvents that are present in the mixture, the team at Henkel were unable to reveal the identity of the other ingredients that comprise the formulation. In light of this, the thermal stability of the GM has been studied in isolation (i.e. as a pure film) on a mild steel substrate. This sample environment is intended to act as a simulation for that in which the GM is used in industry. The substrate has been ground and polished to a mirror finish in order to simplify the experimental acquisition and interpretation of the data.

In order to get the clearest picture possible, both Raman and IR spectromicroscopy were used.

Following on from the in-situ analysis of the GM in the model application environment, the changes induced by heating the GM to the application temperature of 160 °C were recorded using proton and $^{29}$Si NMR. In the case of the $^{29}$Si spectra, polarization transfer was required in order to increase the sensitivity of the experiment and decrease the acquisition time required to collect data.[1] This was achieved using a refocused ‘insensitive nucleus enhancement by polarization transfer’ (INEPTRD) pulse sequence, the theoretical outline of which is presented in Chapter 2. The INEPTRD pulse sequence was based on a template provided on the NMR software and this was optimised for the system under examination.
The changes in the proton and $^{29}$Si NMR spectra of the GM were also recorded as a function of temperature. Unfortunately, the temperature was limited to a maximum temperature of 130 °C on the heating probe in the spectrometer available for the work.

3.2 Experimental

3.2.1 Introduction

The results for two distinct sample sets presented in this chapter and the sample preparation and analysis details are presented here.

Experimental subsections 3.2.2 to 3.2.4 relate to the preparation of GM coated mirror polished mild steel substrates and their subsequent analysis using vibrational (FTIR and Raman) microspectroscopy.

Experimental subsections 3.2.5 and 3.2.6 relate to the preparation of GM samples in solution and the analysis of these samples using $^1$H and $^{29}$Si NMR. The solution samples of the GM were prepared in DMSO-d$_6$ and $^1$H and $^{29}$Si NMR spectra were recorded at room temperature before and after heating to 160 °C.

Experimental subsection 3.2.7 relates to the analysis of the GM using simultaneous DTA/TGA.

3.2.2 Section 3.3: Sample Preparation

The samples for the IR and Raman in-situ heating experiments were prepared as follows. Mild steel screws with a 1” diameter circular face were grinded with Streurs SiC foil backed grinding paper. The grinding was carried out using decreasing grit size, starting with 120 grain, 500 grain, 800 grain and finishing with 1200 grain. The screws were sonicated in hexane for fifteen minutes in between each step to remove
contamination. The grinding was followed by polishing using 9µm, 3µm & 1µm diamond suspension: Struers DiaDuo. The polishing was carried out using Streurs MD Nap polishing pads, magnetically fixed to the polishing wheel. Separate pads were used for each grade of diamond suspension and the pieces were cleaned thoroughly using sonication in hexane in between polishing steps. The MPMSS samples described in section 3.2.1 were spray coated with a GM/EtOAc solution of 8wt% concentration at the Henkel laboratory. These coated samples were separated into pieces with an approximate area of 0.25cm² for use in heating experiments.

3.2.3 Section 3.3: In-Situ Infrared Heating Experiments

A Linkam heating accessory was used to control the heating of the samples during IR spectromicroscopic analysis. The heating accessory was calibrated by placing a mild steel sample on the heating mantel, recording the temperature at the surface of the mild steel using a Therma Elite surface temperature probe and comparing it with the reading on the Linkam. The calibration graph is given in Error! Reference source not found..
IR spectra were recorded at 10 °C intervals from room temperature to the application temperature of 160 °C. The heating rate applied in between analysis points was 10 °C/min. Samples were allowed to equilibrate for 5 minutes once the target temperature was reached before the recording of spectra. Spectra were recorded using a Perkin Elmer 400N Spotlight FT-IR Microscope. 64 scans were acquired for each spectrum at a resolution 1cm⁻¹. A polished gold plated surface was used to record the background spectrum for each heating experiment. The detector of the Spotlight microscope was cooled using liquid nitrogen prior to each heating experiment. The GM film on the MPMSS surface was protected from contamination using a CaF coverslip. This also minimised thickness fluctuations that occurred in the uncovered GM films during heating. Spectra were recorded in the mid IR region from 750 to 4000cm⁻¹. The interaction area of the IR beam and the sample was 200 x 200 µm. Determination of the thickness of the film analysed during thermal treatment was complicated due to the
transition of the film from crystalline to liquid form at ca. 65 °C. Thickness measurements were taken on films after heating and they were seen to range in thickness from 20±3µm to 63±3µm. This variation in film thickness arose from the necessity to cover the film with either a CaF or glass coverslip after melting of the GM to maintain constant thickness during measurements. This limited the degree of control of the coating film thickness and resulted in the wide range of thickness reported here.

3.2.4 Section 3.3: In-Situ Raman Heating Experiments

GM coated MPMSS samples prepared in the manner outlined in section 3.2.1 were used to record the Raman spectrum of the GM on MPMSS as a function of temperature. Raman spectra were recorded using a Horiba Jobin Yvon LabRAM HR 800 Raman microscope. The laser line used was the 100mW, 660nm solid state diode laser. Spectra were recorded using a 1% filter on the laser output in order to prevent damage to the GM which was extremely sensitive to laser radiation. A x100 objective was used to record all spectra. 3 accumulations of 40s long exposure times were recorded for each spectrum. A thin glass coverslip was used to protect the GM layer on the MPMSS substrate and also to stop film thickness fluctuations during data acquisition. Heating was carried out using the Linkam accessory and the settings of the heating platform were the same as those outlined for the IR heating experiments outlined in section 3.2.2.

3.2.5 Section 3.4: Sample Preparation

Table 3-1 shows the masses recorded for the samples prepared for the before/after heating experiment (section 3.4.1).
<table>
<thead>
<tr>
<th>Alkoxysilane</th>
<th>Mass (g)</th>
<th>Solvent Mass (g)</th>
<th>GM wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>GM</td>
<td>0.592</td>
<td>0.636</td>
<td>48.21</td>
</tr>
<tr>
<td>GM</td>
<td>0.056</td>
<td>1.155</td>
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</tr>
<tr>
<td>GM</td>
<td>0.096</td>
<td>1.085</td>
<td>8.13</td>
</tr>
</tbody>
</table>

Table 3-1: Masses and calculated concentration of the alkoxysilanes and solvent used to prepare the samples for the stability test.

For all experiments in this work, the GM used was kept in ethyl acetate (EtOAc) at 50wt% concentration supplied by Henkel. Before sample preparation, the required volume of the GM was obtained by removing the EtOAc in vacuo. The samples were filtered prior to addition to the NMR tubes. The tubes used were Norell ultra precision select borosilicate glass tubes with 0.0070 concentricity, 0.0190 camber 4.97mm outer diameter and 4.20mm inner diameter.

3.2.6 Section 3.4: NMR Experiments

$^1$H and $^{29}$Si NMR spectra were recorded using a Bruker Avance II 400 MHz spectrometer. The INEPTRD pulse sequence used for the recording of $^{29}$Si NMR spectra is shown in Error! Reference source not found.. The critical parameters that required optimisation for the recording of $^{29}$Si NMR spectra are shown in Table 3-2.
The NMR temperature probe was calibrated using an ethylene glycol samples and monitoring the difference in the chemical shift as a function of temperature.

**Figure 3-2**: The INEPTRD pulse program used to acquire Silicon spectra. The values of the labelled parameters are given in Table 3-2.

**Figure 3-3**: Bruker NMR temperature probe calibration plot
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>PULPROG</td>
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<td>Nuc1</td>
<td>$^{29}\text{Si}$</td>
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<tr>
<td>TD</td>
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<td>$^{1}\text{H}$</td>
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<td>PL2 (dB)</td>
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<td></td>
</tr>
<tr>
<td>TD0</td>
<td>576</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3-2: The parameter settings for the INEPT RD pulse program used to record silicon spectra. The value TD0 describes the number of repetitions of scans for a given experiment and in this case indicates the number required for a 12hr acquisition.
3.2.7 Section 3.5: Thermogravimetric analysis

Thermogravimetric analysis was carried using a Shimadzu DTG 60 instrument. Experiments were carried out in air. The pure GM was analysed after removal of ethyl acetate. The sample was heated at a rate of 1 °C per minute to a temperature of 175 °C. It was held at this temperature and allowed to cool.

3.2.8 Materials and Equipment


Metallurgical supplies were sourced form Mason Technology, 228 S Circular Rd, Merchants Quay, Dublin.

Linkam heating accessory supplied by the technical team: Focas Institute, DIT Kevin St., Dublin 8.


NMR solvents supplied by:

- Sigma-Aldrich Ireland Limited, Vale Road, Arklow, Wicklow, Ireland.
- Apollo Scientific Ltd, Unit 3 & 4, Parkway, Denton, Manchester, M34 3SG, UK
3.3 Results: Vibrational Spectroscopy

3.3.1 In-situ Infrared Spectroscopy

Figure 3-4: The FTIR spectrum of the GM coating on MPMSS. The peaks of interest are labelled and identified in the text.

The peaks labelled in Error! Reference source not found. were assigned as follows:

- (I): the urethane secondary amine stretch: 3354cm\(^{-1}\)
- (II): the C-H stretch vibrations: 2888cm\(^{-1}\), 2929cm\(^{-1}\) & 2975cm\(^{-1}\)
- (III): the carbonyl group absorption: 1724cm\(^{-1}\)
- (IV): the symmetric stretch of the aromatic ring: 1603cm\(^{-1}\)
- (V): the nitroso group absorption: 1383cm\(^{-1}\)
Of the peaks assigned above the urethane secondary amine stretch absorption yielded the most useful information during heating experiments. Layers of the GM on mirror polished mild steel substrates were heated to the application temperature (160 °C) and the spectra recorded at intervals of 10 °C. The layer was allowed to equilibrate with the heating mantel for 5 minutes prior to recording of the spectra. The following figure shows the manner in which the urethane secondary amine absorption peak changed at elevated temperature.

![Figure 3-5: The change in the urethane secondary amine stretch ($\nu_s$(N-H)) as temperature of the GM increases.](image)

Error! Reference source not found. shows that the urethane secondary amine may absorb at three different wavenumbers depending on the temperature at which the spectrum of the GM is recorded. The urethane peak shown here at 150 °C contains
overlapping peaks and these were better resolved by finding the second derivative of the GM spectrum.

![Second derivative spectra of ν\textsubscript{s}(N-H)](image)

Figure 3-6: The second derivative spectra of ν\textsubscript{s}(N-H) shown in Error! Reference source not found.. In Figure 3-6, the second derivative spectra of the urethane secondary amine stretch absorption are shown. At room temperature, the GM is a crystalline solid and the absorption peak of the urethane secondary amine occurs 3245 cm\textsuperscript{-1}. This indicates that the GM is involved in polymeric hydrogen bonding in the crystalline state. Upon melting (at ca. 65 \degree C), the spectrum of the liquid GM shows that the urethane secondary amine stretch absorption has shifted to 3347 cm\textsuperscript{-1}. Absorption at this wavenumber indicates that the GM hydrogen bonding is dominated by dimeric associations and the
polymeric hydrogen bonding is no longer detected. As the temperature of the GM approaches the application temperature the absorption peak associated with the hydrogen bonded dimer decreases in intensity. This change is accompanied by the increase of absorption at 3456 cm$^{-1}$. This absorption is that of the free urethane amine and indicates that heating has interrupted the hydrogen bonding via the urethane amine and carbonyl. [2]

Unfortunately, the region of the GM FTIR spectrum in which the vibrational transitions of the alkoxy silane groups are found overlaps with several other low wavenumber absorptions. A better indication of what happens at the alkoxy silane moiety during heating of the GM was found using Raman spectroscopy.
3.3.2 *In-situ* Raman Spectroscopy

Figure 3-7: The disiloxane peak of the GM. The peak is found at $557\text{cm}^{-1}$. The spectra have been offset for the sake of clarity.

The Raman spectroscopy of the GM revealed the formation of a $T^1$ disiloxane bond at the alkoxy silane moiety as the temperature of the sample increased. The scattering of this symmetric bond results in a strong peak in the Raman spectrum. The wavelength of the peak with which it is associated is $557\text{cm}^{-1}$.

Analysis of compounds containing disiloxane bonds have shown that this scattering falls in the range of $550\text{cm}^{-1}$-$600\text{cm}^{-1}$.[3]
As the temperature of the GM increases, the intensity of the disiloxane peak increases also. It reaches a maximum intensity in the region of 130 °C, above which the intensity drops. This has been interpreted as indicating further condensation of the T\(^1\) disiloxane to condensates of higher Si content such as T\(^2\) or T\(^3\).

### 3.3.3 In situ Vibrational Analysis of the GM during heating

![Vibrational Analysis of the GM](image)

**Figure 3-8**: Comparison of the formation and consumption of disiloxane and the intensity of the absorption of the free urethane secondary amine as a function of temperature.

The compiled results from multiple experiments where the GM was heated on a mild steel surface are shown in Figure 3-8. It must be noted that at each temperature point during recording of the spectra that the GM was allowed to equilibrate for at least 5 minutes. The intensity of the disiloxane peak increases as the temperature is increased from 90 – 130 °C. The rate of change also appears to increase in this temperature.
interval. After the peak intensity of the disiloxane bond is recorded at 130 °C, the intensity falls sharply. It is proposed that this is due to consumption of the disiloxane dimers as they interact and form condensates of higher order.

Figure 3-9: The disiloxane or T\textsuperscript{1} GM condensate is the common species below 130 °C. Above this temperature, higher order condensates are believed to form. This process is associated with the thermal breakdown of the urethane hydrogen bond.

The free urethane secondary amine absorption increases linearly as the temperature increases however the rate of increase plateaus at 150-160 °C. It is proposed that the interruption of the linear increase of the change in intensity of the free urethane secondary amine results from the change in behaviour of the GM condensation above the threshold temperature of 130 °C. Higher order (i.e. >T\textsuperscript{1}) condensates may facilitate a reversion to the hydrogen bonded state. This will result from the close proximity in which the organofunctional moieties of the GM are found on the high order siloxanes. The change in the urethane hydrogen bonding of the GM was not reversible due to the thermally induced condensation of the GM. The hydrogen bonding before and after heating is presented in the following section. Condensation of the GM precludes the return of the material to the crystalline state on cooling as observed prior to heating at <\textit{ca.} 65 °C and hence the polymeric hydrogen bonding state discussed in section 3.3.1.
3.3.4 Infrared Spectroscopy: Comparison of the GM before and after Heating

Figure 3-10: (A) The spectrum of the crystalline GM before heating. (B) The spectrum of the GM after heating. Spectra recorded at room temperature.

The 750-1200 cm$^{-1}$ region of the spectrum associated silyl ether, silanol and siloxane bonding contains overlapping contributions from the urethane moiety of the GM. Therefore it is difficult to make any definite assertions based on these bands about how much hydrolysis and condensation play a role in the compound after heating using the IR spectrum. However, the vibration bands associated with the urethane secondary amine and its associated hydrogen bonding can be used to make some qualitative remarks on the GM condensation. Before heating, the GM is crystalline and the urethane hydrogen bonding indicates a polymeric association between neighbouring molecules. After heating, the urethane secondary amine band exhibits absorption at
3334cm\(^{-1}\). This peak is associated with the dimeric hydrogen bonded urethane secondary amine. It is proposed that this change in the spectrum indicates that the GM has undergone condensation to some degree. The molecules in the GM after heating are no longer permitted to adopt the polymeric hydrogen bonding state upon cooling, due to formation of siloxane bonds which prevent the close proximity of the molecules required for polymeric association. Figure 3-11 presents images comparing the GM in its crystalline state before heating and the state in which it is found having been allowed to cool after heating.

![Figure 3-11: (A) The GM in its crystalline state on a mirror polished mild steel surface prior to heating analysis. (B) The GM after heating. Crystallization has occurred however there is also a particulate structure to the compound after heating. The vertical edge of the images is ca. 200µm.](image)

The second peak at 3414cm\(^{-1}\) is interpreted as being that of silanols formed during heating. Initially it was thought that this peak was associated with the free urethane secondary amine absorption but there are two reasons to abandon this interpretation. If the free amine is present then there must also be free carbonyl groups present in the compound. The absorption peak for the urethane carbonyl shifts to a higher wavenumber as hydrogen bonding is interrupted. The hydrogen bonded carbonyl absorbs at ca. 1700cm\(^{-1}\) and the free carbonyl absorbs at ca. 1730cm\(^{-1}\). The absorption
for the GM after thermal treatment is compared to that of the GM at 160 °C. There is no contribution of the free carbonyl to the absorption of the carbonyl in the spectrum of the GM taken after heating. This observation supports the argument that the amine absorption at 3414 cm\(^{-1}\) is not associated with a urethane free amine stretch.

Figure 3-12: A comparison of the GM carbonyl absorption in spectra taken at elevated (160 °C) and room temperature. The room temperature spectrum is taken after the GM has been subjected to heating to 160 °C and allowed to cool.

### 3.4 Results: Proton and \(^{29}\)Si NMR Spectroscopy

#### 3.4.1 GM: Before and After Heating to 160 °C

The GM was dissolved in DMSO-d6 at loadings of 48.2 wt%, 8.1 wt% and 4.6 wt%. This solvent was chosen due to its high boiling point of 189 °C. \(^{29}\)Si NMR spectra were
referenced against that of the unhydrolysed GM. The notation used when referring to the chemical environment of the silicon atom in the $^{29}$Si NMR follows the classical T notation. In this format, T is used to indicate that the silicon atom is bonded to three oxygen atoms. Superscripts $i$ and $j$ usually accompany the T notation ($T_{ij}^{ij} i, j = 0, 1, 2 \text{ or } 3$) where $i$ indicates the number of oxo bridges Si-O-Si and $j$ indicates the number of hydroxy groups. Generally, the identification of the number of hydroxyl groups is uncertain and in these cases the $j$ superscript is omitted. In the results presented here, the $i$ superscript is retained as the identification of oxo bridges is known.
3.4.1.1 Assignment of the GM \(^1\text{H}\) Spectrum of the GM

Figure 3-13: The \(^1\text{H}\) spectrum of the GM recorded in DMSO-d6 at 8.1wt%.

Figure 3-14: The GM structure and labelled protons

The assignment of the GM \(^1\text{H}\) spectrum is shown in Figure 3-13 and Figure 3-14. Overlapping proton signals include the methyl signals of A and J and the methylene signals of B and I. In-plane “flipping” of the nitroso group results in a complex peak response for the methine protons associated with the aromatic ring, K and L. A broad peak results for the proton labelled K and the proton peak of L is broadened to the point of being barely indistinguishable from the baseline of the spectrum. In the following sections the
manner in which the concentration of the GM affects its hydrolysis and condensation reactions when exposed to thermal stress will be presented.

3.4.1.2 48.2 wt% GM-DMSO-d6

The 0-4ppm region of the GM-DMSO-d6 spectrum is shown in Figure 3-15.

![Figure 3-15: 0-4ppm range of the proton NMR of the GM-DMSO-d6, 48.2 wt% sample before (A) and after (B) heating to 160 °C.](image)

In Figure 3-15, ‘I’ indicates a water peak from the DMSO-d6 that is absent spectrum B. ‘II’ & ‘III’ indicate peaks at 3.448ppm and 1.07ppm relating to the ethanol methylene and the methyl protons respectively. From this region of the spectrum it may be seen that the ethanol evolved during the hydrolysis reaction has remained in the GM DMSO-
d6 sample after cooling to ambient temperature. The water that was contained in the DMSO-d6 has been consumed during the heating experiment.

![Proton NMR spectra](image)

**Figure 3-16**: 4-8ppm range of the proton NMR of the GM-DMSO-d6, 48.2wt% sample before (A) and after (B) heating to 160 °C.

In Figure 3-16, ‘I’ indicates a silanol peak at 6.521ppm. ‘II’ indicates a peak at 4.308ppm relating to the ethanol hydroxyl. The ethanol hydroxyl peak is shifted from its usual position at 4.63ppm in DMSO-d6, up-field to 4.307ppm.[4] This indicates that there is an intermolecular process involving the ethanol in the GM DMSO-d6 solution.
Figure 3-17: (-30) to (-60)ppm range of the $^{29}$Si INEPTRD NMR of the GM-DMSO-d$_6$, 48.2wt% sample before (A) and after (B) heating to 160 °C.

In Figure 3-17, ‘I’ indicates a silicon peak at -43.87ppm that is present in the ‘before’ spectrum and at a higher intensity (II) in the after spectrum. This peak is a silanol peak of the hydrolysed GM. The peaks indicated by labels ‘III’ and ‘IV’ are those related to the T$^1$ condensate of the GM produced during heating. The peaks are very weak in comparison to the parent monomer peak and it can be assumed that the extent of condensation in the GM is limited. In order to get a clearer picture of these weaker condensate signals, a long duration, multiple scan experiment was run which is shown in Figure 3-18.
Figure 3-18: The high resolution scan of the 48.2wt% GM-DMSO-d6 sample after heating to 160 °C.

In Figure 3-18, the key finding is the presence of the peak labelled ‘I’, related to the T\textsuperscript{2} condensate of the GM. It is also necessary to remark on the presence of a variety of peaks in the range at which silanol resonances are expected. These minor peaks, labelled ‘II’ to ‘V’, are in excess of the stronger silanol peaks indicated in Figure 3-16. This results in 6 silanol peaks present for the GM which exceeds the expected 3. It is proposed that this excess of silanol peaks results from the intermolecular bonding state of the parent molecule. There are two explanations that may be applied to this observation. The first is that the peaks result from silanols borne by hydrolysed GM molecules that are engaged in urethane hydrogen bonding and those that are not: the intermolecular bonding state having an effect on the silanol chemical shift. The second is that the urethane bonding between GM T\textsuperscript{0} monomers and T\textsuperscript{1} and T\textsuperscript{2} oligomers has an
effect on the chemical shift of the silanols present in solution. Either argument has validity when the extreme sensitivity of the silicon NMR chemical shift to its environment is taken into account.

3.4.1.3 8.1wt% GM-DMSO-d6

Figure 3-19: 0-4ppm range of the proton NMR of the GM-DMSO-d6, 8.1wt% sample before (A) and after (B) heating to 160 °C.

In Figure 3-19, the peaks I, II and III indicate the same water and ethanol peaks as those labelled in Figure 3-15. Similar to the 48.2wt% sample, the water has been fully consumed during the heating experiment. The intensity of the ethanol peaks indicates that the amount of ethanol evolved is larger than that in the sample prepared at 48.2wt%. The peak at 0.429ppm labelled ‘IV’ is related to the methylene group attached to the Si atom. The up-field shift of this peak is caused by the hydrolysis of the GM and...
it is resolved more clearly in this spectrum. This is due to the higher extent of hydrolysis that has occurred in this sample relative to the 48.2wt% sample.

Figure 3-20: 4-8ppm range of the proton NMR of the GM-DMSO-d6, 8.1wt% sample before (A) and after (B) heating to 160 °C.

Labels ‘I’ to ‘IV’ in Figure 3-20 show that the variety of silanols detected for this sample is more varied than that of the 48.2wt% sample. The peak labelled ‘V’ is that of the ethanol hydroxyl group. In both Figure 3-19 and Figure 3-20 the multiplicity of the proton peaks of the GM can be seen to be poorly resolved in the ‘after’ sample compared to the ‘before’ sample. This diminished resolution is also found for proton spectra of the GM with high concentration regardless of whether the sample has been heated or not.
Figure 3-21: (-30)-(60)ppm range of the $^{29}$Si INEPTRD NMR of the GM-DMSO-d$_6$, 8.1wt% sample before (A) and after (B) heating to 160 °C. The monomer peak is detected at -45.38ppm.

The intensity of the silanol peaks at -42.87ppm (I) and -43.89ppm (II) is higher relative to the parent monomer peak when compared with the relative intensity of the silanol and monomer peaks detected for the 48wt% sample. This indicates that the extent of hydrolysis for the 8.1wt% GM-DMSO-d$_6$ sample is higher than that of the 48.2wt%.

The monomer peak is also less intense in the ‘after’ spectrum than that of the 48.2wt% further supporting the idea that this sample has hydrolysed to a greater extent. The peaks labelled ‘III’ and ‘IV’ are those of the $T^1$ condensate and these are better resolved in the scan presented in Error! Reference source not found.
Figure 3-22: The high resolution scan of the 8.1wt% GM-DMSO sample after heating to 160 °C.

No T\textsuperscript{2} condensate peak was detected in the high resolution scan of the 8.1wt% sample. The number of silanol peaks detected exceeds 3 similar to the case of the 48.2wt%. The T\textsuperscript{1} condensate peaks show a mixture of silanol and alkoxy silicone substitution on the silicon atoms of the oligomers that have formed.
3.4.1.4 4.6wt% GM-DMSO-d6

Figure 3-23: 0-4ppm range of the proton NMR of the GM-DMSO-d6, 4.6wt% sample before (A) and after (B) heating to 160 °C.

The spectra in Figure 3-23 follow the trends that have already been observed for the 8.1wt% and 48.2wt% samples. The 8.1wt% sample indicated that the extent of hydrolysis was more complete than in the case of the 48.2wt% sample. This is seen again for the 4.6wt% sample. The relative intensity of the peaks associated with the ethanol generated during hydrolysis and those of the GM is higher again than that observed for the 8.1wt% sample.
Figure 3-24: 4-8ppm range of the proton NMR of the GM-DMSO-d6, 4.6wt% sample before (A) and after (B) heating to 160 °C.

The number of silanol peaks detected in the range of 5.8-6.8ppm is dramatically increased for the hydrolysed GM in the 4.6wt% sample. The hydrolysis of the GM is seen to be more complex in comparison with the samples prepared at higher concentration.
Figure 3-25: (-30)-(-60)ppm range of the $^{29}$Si INEPT RD NMR of the GM-DMSO-d6, 4.6wt% sample before (A) and after (B) heating to 160 °C.

In Figure 3-25, the intensity of the precursor peak has dropped close to zero in the ‘after’ sample. The high resolution spectrum of the GM presented in Error! Reference source not found. will give a better idea of the complexity of the hydrolysis and condensation products of the heated 4.6wt% GM DMSO-d6 sample.
Figure 3-26: The high resolution scan of the 4.8wt% GM-DMSO sample after heating to 160 °C.

The number of smaller peaks adjacent to and downfield from the strong $T_1^\perp$ peak at 50.57ppm is thought to be a result of intermolecular interactions between GM monomers and oligomers produced by the hydrolysis and condensation reactions.
3.4.2 GM Dynamic Heating Experiment; 25 °C to 130 °C

Figure 3-27: The 4-10ppm region of the proton spectrum of the GM as a function of temperature. The peak marked with an asterisk is that of the urethane secondary amine proton.

In Figure 3-27, the peak of the urethane secondary amine proton is seen to shift up-field as the temperature of the sample increases. At 50 °C the peak is detected at 7.164ppm and at 130 °C it is detected at 6.426ppm. An explanation for this peak shift is that it relates to the change in the urethane secondary amine proton environment as hydrogen bonding between the amine and the urethane carbonyl becomes affected by the increase in temperature of the sample. In the IR results presented in section 4.2.1 and 4.2.3, it is seen that an absorption band relating to the free urethane secondary amine is detected as the temperature of the GM on the mild steel substrate is increased. The amine proton
will experience less of the de-shielding influence of the carbonyl oxygen atom to which it is hydrogen bonded as the temperature increases thus lowering the frequency at which it is found in the proton spectrum.

In the same region of the spectrum shown in Figure 3-27, the exchange process related to the nitroso moiety in-plane ‘flipping’ is observed. The process shows the resolution of the peaks at 7.32ppm and 6.895ppm becoming clearer as the temperature of the sample is raised. This has been the subject of several published research articles and is well understood.[5], [6] In the context of this project, it may be inferred from the manner in which the nitroso exchange process is recorded that the nitroso moiety is stable during the heating experiments that have been carried out here. Similarly, in section 3.4.1 the peaks of the protons in the vicinity of the nitroso moiety show the same distortion at room temperature before and after heating, again suggesting that the nitroso moiety remained intact when heated to 160 °C in DMSO-d6.
3.5 Thermogravimetric analysis

Figure 3-28: Thermogravimetric and differential thermal analysis profile of the pure GM.

The DTA profile of the GM contains three different thermal events. The first is an endothermal event which is complete at 70 °C. This endothermal event is very likely to be the result of the evaporation of residual ethyl acetate. Next, there is a gradual exothermal event occurring between 70 °C and 140 °C. This is indicative of the formation of the siloxane in the GM which is moderated by the urethane hydrogen bonding. This is followed by a significant exothermal event beginning at 140 °C which is not completed within the temperature range of the data shown here. The urethane hydrogen bonding ceases to be dominant in the pure GM and condensation and hydrolysis of the silane moiety begins to occur more easily.
3.6 Conclusions

3.6.1 Vibrational Spectroscopy

The vibrational analysis of the GM in a simulated application environment has revealed the following.

![Diagram showing the transition from polymeric to dimeric hydrogen bonding, to the non-bonded monomer. The absorption frequency of the urethane secondary amine stretch increases as the hydrogen bonding is interrupted.](image)

Figure 3-29: The transition from polymeric to dimeric hydrogen bonding, to the non-bonded monomer. The absorption frequency of the urethane secondary amine stretch increases as the hydrogen bonding is interrupted.

The IR characterization of the GM allowed for the identification of a contribution to intermolecular bonding by the urethane group. There are three different hydrogen bonded states of the GM, as shown in **Error! Reference source not found.**. As a crystalline solid at room temperature, the GM is involved in polymolecular hydrogen bonding through the interaction of the secondary amine and carbonyl groups of the urethane moiety in separate molecules. On melting, this association changes and the intermolecular bonding is limited to a dimeric form. As the temperature of the GM increases, the hydrogen bonding begins to break down and the free urethane secondary amine is detected.[2]
The urethane hydrogen bonding is responsible for the stabilization of the disiloxane-based GM condensate. Large molecular weight substituent groups attached to the silicon atom reduce the rate of hydrolysis of alkoxy silanes. This is due to steric hindrance which interferes with the formation of the pentacoordinate intermediate which is integral to the mechanism of the hydrolysis reaction. It is reasonable to assume that intermolecular dimer associations between the substituents of alkoxy silane coupling agents will act to amplify steric hindrance and reduce the rate of hydrolysis. Similarly, condensation between the molecules that comprise a dimer will be favoured as the probability for interaction of the silanol groups will be higher.

After heating, the molecules of the GM at room temperature exhibit a dimeric association in contrast to the polymolecular association exhibited by the GM prior to heating. This is proposed to indicate the condensation of the GM during heating. The network formed by siloxane bond formation prevents the polymolecular hydrogen bonding association from occurring as the molecules are restricted from being in the necessary proximity to allow this association to occur.

3.6.2 Proton and $^{29}$Si NMR Spectroscopy

The results from the thermally treated samples of the GM indicate that the urethane hydrogen bonding plays an active role in the hydrolysis and condensation reactions of the GM under thermal stress. At high concentration (48.2wt%) the GM monomer is more stable and is not as prone to hydrolysis when compared to the samples at lower concentrations. It is believed that this is a result of the urethane hydrogen bonding which stabilises the GM to hydrolysis when it is at a high concentration. As the concentration of the GM decreases, the stabilising effect of the hydrogen bonding also decreases. The GM monomer in low concentration samples is more susceptible to hydrolysis as we can see from the spectra where the intensity of the GM monomer peak
decreases significantly in the thermally treated samples. The condensation of the hydrolysed GM is also concentration dependent: at high concentration, the hydrolysed GM condenses to form higher order condensates than the samples in which the GM concentration is low.

Figure 3-30: A comparison of the $^{29}$Si INEPTRD spectra of the thermally treated samples of the GM at the 3 concentrations examined.

In order to explain the manner in which the GM hydrolyses and condenses the following is proposed. The GM exists as an equilibrium between urethane hydrogen bonded dimers and monomers that are not engaged in hydrogen bonding. The concentration of each is constant and also depends on the concentration of the sample. The higher the concentration of the sample, the more GM monomers that are found in the hydrogen bonded state. [2] When hydrolysis induced by heating begins to occur, the free monomers are those that are consumed first by the hydrolysis reaction. The
consumption of the free monomers reduces the concentration of the GM overall and results in the production of more free monomers that are subsequently consumed. It has been shown that the unhydrolysed GM monomer is consumed by heating to a higher degree as the concentration of the GM solution decreases. The stability of the GM at higher concentrations relies on the fact that a higher percentage of the compound is stabilised by hydrogen bonding therefore reducing the amount of the monomer consumed by hydrolysis induced by heating.

In addition to this behaviour, it was also seen that the hydrolysed GM at high concentration condenses to higher order condensates. This would indicate that the general behaviour of the reactivity of the condensates is not dictated by hydrogen bonding and that the hydrolysates condense more completely in the higher concentration sample as expected.
3.7 References


Chapter 4: GM-Substrate Interaction under Thermal Stress

4.1 Introduction
As outlined in the opening chapter (section 1.8), the GM is used as part of a formulation on a variety of substrates. The simplest substrate to which the GM is applied is mild steel. An example of a more complex substrate is the zinc phosphate conversion coated mild steel substrate. The project partners in Henkel have indicated that the behaviour of GM containing formulation differs depending on the substrate to which it is applied. The changes that occur in the GM as a result of thermal stress have been presented in chapter 3. It was shown that the GM hydrolyses and condenses when subjected to thermal stress. This was observed for both solution experiments and in-situ vibrational analysis of the GM in isolation on a mild steel substrate. It is reasonable to expect that the hydrolysates and condensates produced by thermal stress will interact with the substrate surface. In the case of the mild steel surfaces the analysis was straightforward as the substrate plays a passive role during the prebake process. Therefore, sample surfaces that had been exposed to thermal treatment in the presence of the GM were analysed directly. The case of the ZPCC samples is more complex. From the literature it was revealed that that ZPCCs dehydrate when exposed to thermal stress and this process itself is complex.[1] The ZPCC is comprised of more than one type of zinc phosphate compound, each of which may behave differently when subjected to thermal stress. In-situ analysis of the interaction of the ZPCC with the GM similar to that carried out for the GM-MPMSS surface in chapter 3 was attempted. The overlapping infrared absorption of the GM and ZPCC materials precluded the recording of any meaningful results from this process however. Therefore, the characterisation of the ZPCC coating presented here deals primarily with the dehydration of the coating due to thermal stress.
4.2 Experimental

4.2.1 Section 4.3: Sample Preparation

Segments of mild steel lap (supplied by Henkel) were set in epoxy fixative. The lap surface was ground with 120, 600 and 1200 grit SiC paper. They were then polished using 9µm, 3µm and 1µm Struers diamond polishing suspension and MD Nap soft polishing cloths. Once freed from the epoxy fixative, the unpolished surfaces were ground using a hand polishing tool to remove any remaining epoxy. Samples were then sonicated in ethyl acetate for fifteen minutes. Before coating, samples were stored in a dessicating vessel containing cobalt chloride salt.

10µL of 3.125%w/w GM in EtOAc was applied to the polished surface. Film formation was achieved using a Sheen Filmfuge 1110 spin coater. A rotation speed of 1000rpm was applied for 40s. Samples were then stored in a dessicating vessel.

4.2.2 Section 4.3: EDX

EDX analysis was carried out using an Oxford Instrument INCA X-MAX Energy Dispersive X-ray Spectrometer. After thermal analysis the elemental composition of the MPMSL surface was analysed. A sample untreated with the GM was compared with a sample that had been thermally treated with a GM coating. The samples were mounted on an aluminium stub and introduced to the specimen chamber without any coating as this was unnecessary given the conductivity of the substrate. The accelerating voltage of the electron beam used for analysis was 5kV. This voltage was chosen as it was sufficient to excite the x-ray emission of interest. The lower voltage also has better surface specificity than higher exciting voltages as it exhibits a reduced interaction volume at the surface. The INCA mapping software was used. X-ray spectra were
recorded at five different sites at each surface. The magnification for the mapping was x2k.

4.2.3 Section 4.3: XPS

XPS analysis was carried out by Dr Steve Hinder, University of Surrey. X-ray photoelectron spectrometer measurements were taken with a Thermo VG Scientific (East Grinstead, UK) Sigma Probe spectrometer using a monochromated Al Kα X-ray source (hv = 1486.6 eV). The area analysed was 400µm in diameter. Measurements were recorded at 37° to the plane of the sample surface.

4.2.4 Section 4.3: AFMIR

Measurements were carried out by Anirban Roy and Kevin Kjoller at Anasys instruments Corp., Santa Barbara, CA, USA. Measurements were recorded using the Anasys NanoIR2 instrument. The samples were examined in the Resonance enhanced mode on a nanoIR2 system equipped with a QCL laser as the IR source. The spectra were acquired over the 900 – 1800 cm⁻¹ range with a spectral resolution of 2 cm⁻¹. Acquired spectra were averaged and filtered using a De-glitch filter.

4.2.5 Section 4.4: Sample Preparation

Gardobond 985+ deoxylyte treated ZPCCs were analysed in this section of the work. 958+ ZPCC coated mild steel laps were supplied by staff at the Henkel laboratory. Samples were sonicated in deionised water and characterised after drying using a handheld dryer with a cold air flow.

4.2.5.1 Section 4.4: IR Characterization

Spectra of the ZPCC surface were recorded using a Perkin Elmer Spotlight 400N FT-IR Microscope. ZPCC samples were analysed after sonication in deionised water. The background spectrum used for the analysis was taken from a polished gold surface
supplied with the spectrometer. Heating of the sample in 10 °C steps at a rate of 10 °C per minute from room temperature to 150 °C was performed using the Linkam Heating Accessory.

4.2.6 Section 4.4: Raman Spectroscopy

Raman spectra were recorded using a Horiba Jobin Yvon LabRAM HR 800. Spectra were recorded using 300gr/mm grating. 660nm wavelength laser radiation was used and a 10% intensity filter applied in order to avoid thermal damage. A long focal length x100 objective was used to record spectra. Typical exposure time used was 60s and 3 accumulations were recorded to eliminate peaks resulting from interference during spectrum acquisition. The Linkam heating accessory was used to record spectra during heating experiments. Settings of the Linkam were the same as those outlined for the acquisition of Infrared spectra during heating.

4.2.7 Section 4.4: EDX

EDX analysis was carried out using an Oxford Instruments INCA X-MAX Energy Dispersive X-ray Spectrometer. EDX maps of the 958+ coating surface were recorded for thermally treated samples and those as received for comparison. Samples were coated with Carbon using the Cressington Carbon Evaporation Coater 208C. The electron beam voltages used were 7kV and 20kV. Elemental mapping was recorded using the INCA software. The magnification used to map each site was x4k.

4.2.8 Section 4.5: ZnCl₂-GM complex

100ml of 0.01M of ZnCl₂ in methanol and 100ml of 0.02M of GM in methanol were mixed in a round bottom flask. The methanol was removed in vacuo. During this process the red GM-ZnCl₂ complex was formed.
4.2.9 Materials and Equipment


Metallurgical supplies were sourced from Mason Technology, 228 S Circular Rd, Merchants Quay, Dublin.

4.3  The interaction of the GM and the Mild Steel Substrate

The surface of samples that had been used for Raman and IR analysis as a function of temperature were analysed using XPS, EDX and AFM-IR. These samples were from the initial studies on the interaction of the GM and mild steel. The substrate consisted of a mirror polished mild steel lap (MPMSL). The samples in question were heated to a temperature of 150 °C and allowed to cool. The GM layer was removed from the surface of these samples after heat treatment using sonication in the carrier solvent ethyl acetate. It is important to note that the mild steel surface appeared to be unchanged once the GM had been removed i.e. no visible coating or layer remained on the substrate and it retained its mirror finish. The aim of the surface analysis was to establish if any covalent interaction between the GM and the mild steel had occurred.

4.3.1  Energy Dispersive X-Ray Spectroscopy

The surface of the thermally treated GM/MPMSL and that of an untreated control were analysed using EDX.

The accelerating voltage of the electron beam was set at a level (5kV) that would induce photoemission at the surface of the elements of interest without sacrificing surface specificity. Modelling with Casino software indicates that the limit of the interaction depth of an electron accelerated using a 5kV potential is approximately 70nm whereas a 20kV potential will result in an interaction depth of 500-600nm (Figure 4.1 & Figure 4.2).
Figure 4.1: Casino software modelling of the interaction between a 5kV electron beam and a steel substrate covered in a 10nm thick oxide layer. The bulk of the electrons penetrate to \textit{ca.} 70nm below the sample surface.

Figure 4.2: The results for the 20kV electron beam reaction. The bulk of the electrons penetrate to \textit{ca.} 550nm below the sample surface.
Mapping was used so that each recorded number of counts can be considered to be the average taken from a surface analysed at x2k magnification. The results are shown in below (Table 4-1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>C Kα (0.277keV)</th>
<th>Si Kα (1.739keV)</th>
<th>Fe Kα (0.704keV)</th>
<th>O Kα (0.524keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1677</td>
<td>1028</td>
<td>30612</td>
<td>4495</td>
</tr>
<tr>
<td>A2</td>
<td>1619</td>
<td>1090</td>
<td>30730</td>
<td>4410</td>
</tr>
<tr>
<td>A3</td>
<td>1698</td>
<td>1039</td>
<td>30223</td>
<td>4412</td>
</tr>
<tr>
<td>A4</td>
<td>1739</td>
<td>1040</td>
<td>30461</td>
<td>4415</td>
</tr>
<tr>
<td>A5</td>
<td>1663</td>
<td>1000</td>
<td>30552</td>
<td>4175</td>
</tr>
<tr>
<td>B1</td>
<td>1899</td>
<td>1108</td>
<td>30982</td>
<td>5694</td>
</tr>
<tr>
<td>B2</td>
<td>1899</td>
<td>1117</td>
<td>30862</td>
<td>5725</td>
</tr>
<tr>
<td>B3</td>
<td>1826</td>
<td>1083</td>
<td>30505</td>
<td>5655</td>
</tr>
<tr>
<td>B4</td>
<td>1866</td>
<td>1047</td>
<td>30873</td>
<td>5559</td>
</tr>
<tr>
<td>B5</td>
<td>1901</td>
<td>1080</td>
<td>31150</td>
<td>5729</td>
</tr>
</tbody>
</table>

Table 4-1: Detector counts recorded at each X-ray emission energy. Five sites were analysed for each of the untreated MPMSL (A) and the thermally treated GM/MPMSL surface. The average increase of the C signal was 1990 counts and that of the O signal was 1291 counts. The area of interaction for each site was 3024 µm².

Using a simplistic model of the condensation of the silane at the MPMSL surface, for each molecule of GM bound to the surface or integrated into a condensation network formed at the surface, there will be one Si atom, seven O atoms and 13 C atoms present. This excludes any possibility of molecular scission of the GM during the thermal treatment. Therefore, it is expected that the O and C signal increase should be easier to
detect than that for the Si. As a qualitative analysis, this set of data indicates that there is a consistent increase of C and O signals at the surface of the thermally treated GM/MPMSL surface. However the analysis is inconclusive and this increase in C and O signals could be due to an increase in the amount of oxide at the surface. The heating experiments were carried out in an ambient atmosphere and it is not expected that the liquid layer of GM will act as any kind of barrier to the interaction of the heated metal surface and oxygen in its vicinity.

4.3.2 X-ray photoelectron spectroscopy

The atomic % of each of the elements detected on the surface of the MPMSL sample before and after thermal treatment is shown in Table 4-2.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Binding energy (eV)</th>
<th>At. % Before TT</th>
<th>At. % After TT</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s</td>
<td>284.97</td>
<td>36.9</td>
<td>48.9</td>
</tr>
<tr>
<td>Fe2p</td>
<td>710.36</td>
<td>8.0</td>
<td>3.6</td>
</tr>
<tr>
<td>N1s</td>
<td>399.96</td>
<td>2.7</td>
<td>4.8</td>
</tr>
<tr>
<td>Na1s</td>
<td>1071.42</td>
<td>2.9</td>
<td>1.2</td>
</tr>
<tr>
<td>O1s</td>
<td>531.56</td>
<td>46.0</td>
<td>37.9</td>
</tr>
<tr>
<td>Si2p</td>
<td>102.32</td>
<td>1.7</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 4-2: Comparison of the At. % of the elements detected at the MPMSL surface before and after thermal treatment (TT).
There is a significant amount of Na detected varying from 2.9% in the sample before thermal treatment to 1.2% in the treated sample. The source of the Na contamination is thought to be the tap water that was used during the grinding of the mild steel surface under preparation.

Assuming the initial, untreated surface is characterised by an oxide of iron that is contaminated with Na from the sample preparation process, the decrease in the atomic percentage of Fe, O and Na may then be interpreted as the untreated surface becoming obscured by another material. The elements that are detected as having increased in atomic percentage, namely Si, C and N, are each associated with the GM. It may then be argued that there is a deposit on the surface of the MPMSL that is similar in elemental composition to the GM. The amount of GM deposited at the surface must be very low as the fluctuations detected here cannot be interpreted as indicating a dramatic change in the composition of the sample surface.

4.3.2.1 The N 1s peak

![Figure 4.3: The Nitrogen 1s peak for the MPMSL on an untreated sample (left) and a treated sample (right). Both peaks have a maximum at 400eV.](image)

From the literature, the binding energy of the N 1s electron in the nitroso group of \( N, N \)-diethyl-\( p \)-nitrosoaniline is 399.7eV. [2] Unfortunately, this binding energy is very similar for many organic compounds containing nitrogen.[3] Therefore it is not clear
from the N 1s peak which of the nitrogen atoms in the GM is responsible for the peak or if it is produced by both.

### 4.3.2.2 The O 1s peak

![O 1s peak](image)

Figure 4.4: The oxygen 1s peak for the MPMSL on an untreated sample (left) and a treated sample (right). The maxima for the 1s signal on the left occur at 529.8eV and 531.6eV. The maxima for the peak on the right occur at 530eV and 531.6 eV.

The peak for the O 1s photoelectron shows a superposition of oxidation states. From the literature, the peak associated with the O 1s electron in the silica network should possess a binding energy of 533.1eV.[4] This overlaps with the binding energy that is expected for the nitroso O 1s electron which has also been reported as 533.1eV.[2] The Carbonyl O 1s binding energy has been previously reported as being 532.33eV.[5]

From visual inspection, an argument could be made for the presence of a slight shoulder in the region of the 533eV in the spectrum of treated sample. However a proper peak fitting analysis of this data is the only reliable way to indicate if there is a peak present at 533eV.
4.3.2.3 The C 1s peak

![C 1s peak](image)

Figure 4.5: The carbon 1s peak for the MPMSL on as untreated sample (left) and a treated sample (right). The maxima for the peaks on the left occur at 285eV and 288.6eV. The maxima for the peaks on the right occur at 285eV, 286.2eV and 288.2eV.

In the XPS spectrum of the thermally treated GM/MPMSL system three peaks appear that are associated with the C 1s electron. The binding energies of these peaks are 285.0eV, 286.2eV and 288.4eV. These are assumed to be related to the saturated carbon, the carbon oxygen single bond and the carbonyl carbon respectively.

4.3.2.4 The Si 2p peak

![Si 2p peak](image)

Figure 4.6: The silicon 2p peak for the MPMSL on as untreated sample (left) and a treated sample (right). The maxima for the peaks on the left occur at 99.2eV and 102.4eV. The maximum of the peak on the right occurs at 102eV.
In the spectrum of the untreated sample, there is evidence for the presence of elemental Si given by the very weak peak at 99.2eV. This peak is absent in the thermally treated sample spectrum. This may be a further indicator that the steel substrate surface has been obscured by GM deposits. The peak at 102.4eV in both spectra is believed to be that produced by the silicates at the surface.[3]

4.3.3 AFM IR

Three MPMSS samples were sent to Anasys for analysis using the AFM IR nanoIR2 instrument. The control sample of the set consisted of a MPMSS sample that had not been exposed to the GM or heat treatment. The other two samples had both been spray coated with the GM and one of these samples had been heated to the application temperature (160 °C). The GM was then removed in the case of both sample surfaces using sonication in ethyl acetate. The aim of the analysis was to determine if the GM formed any kind of covalent bond to the MPMSS surface. The GM treated surface that was not subjected to heat treatment was included to determine if any interaction occurred between the mild steel surface and the GM without the temperature of the sample being raised.
Figure 4.7: (top) IR spectrum taken from the surface of the MPMSS without any exposure to the GM. (bottom) AFM height image of the MPMSS surface.

Figure 4.8: The spectrum taken from the surface of the MPMSS after thermal treatment to 160 °C with a deposited layer of the GM. (bottom) The AFM height image of the thermally treated MPMSS surface.
Unfortunately, the surface of the MPMSS is not an ideal surface for interrogation using AFM IR resonance. The hardness of the surface limits the sensitivity of the tip to thermally induced expansion of materials that exist as thin films on the steel surface. Furthermore, it is likely that there is an interaction between the highly reflective mild steel surface and the electromagnetic radiation provided by the tuneable IR laser that may interfere in the process by which the AFM IR collects data from the surface. A final obstacle is that the amount of GM deposited at the surface is expected to be very low, as indicated by the XPS analysis in section 4.3.2.

4.4 Complex Substrates: Zinc Phosphate Conversion Coating on Mild Steel

The following sections relate to the analysis of the changes that occur in the Henkel 958+ ZPCC when it is subjected to thermal stress. The coating is produced by Henkel and the suffix ‘+’ relates to the application of a deoxylate rinse after the coating has been applied. The deoxylate rinse is a zirconium-based treatment designed to enhance the performance of the coating. In the case of the mild steel samples, the mirror polishing of the substrates allowed analysis of the GM in-situ during thermal stress. It also allowed for easy analysis of the surfaces using the techniques described in the previous section. Unfortunately, this was not the case for the ZPCC samples. The complex surface topography and the vibrational signature of the coating restricted analysis to that concerning the dehydration behaviour of the Henkel coating during thermal stress. The results concerning the dehydration of the Henkel 958+ are presented in the following sections.
4.4.1 Infrared Spectroscopy

The infrared spectrum of the Henkel 958+ was recorded using external reflectance infrared spectroscopy is shown in Figure 4.9.

![Infrared Spectrum](image)

Figure 4.9: External reflectance spectrum of the Henkel 958+ ZPCC

In the region 4000-750cm\(^{-1}\), three main regions of interest are evident. These are 3500-3000cm\(^{-1}\), 1640-1600cm\(^{-1}\) and 1120-900cm\(^{-1}\).

The first two regions contain peaks that result from the vibrations of the water contained within the coating. Those in the upper region (3500-3000cm\(^{-1}\)) are absorption resulting from the stretching vibrations. The peak at 3564cm\(^{-1}\) result from hydroxyl stretching of water molecules incorporated in the coating crystal lattice.[6] Those in the second
region (1640-1600 cm\(^{-1}\)) are those resulting from bending vibrations in the water molecule. [7]

The 1200-900 cm\(^{-1}\) region of absorption is related to \(v_1\) and \(v_3\) vibrations of the PO\(_4\) ion. The peak at 1000 cm\(^{-1}\) is assigned in the literature as being that of the breathing mode, \(v_1\) of the tetrahedral PO\(_4\) ion. The peaks detected at 926 cm\(^{-1}\), 1068 cm\(^{-1}\) and 1120 cm\(^{-1}\) are considered to be those related to the asymmetric stretching of the PO\(_4\) ion, \(v_3\). This mode would generally appear as one peak in spectra acquired for the PO\(_4\) ion in aqueous solution. However, in the crystal structure of the coating, the coordination of the PO\(_4\) ion with its counter cation(s) and the water of crystallization leads to the degeneracy of this mode being disrupted and hence the appearance of three different absorption peaks.[7]

To account for all of the peaks in the 1200-900 cm\(^{-1}\) region of the spectrum, cationic substitution in the matrix must be considered. It is typical in modern zinc phosphating baths to include cations other than Zn such as Mn and Ni. This is known as tricationic zinc phosphating. With the inclusion of these extra cations, the absorption peaks of the PO\(_4\) become further split.[8]

In much of the literature concerning ZPCC, the nature of the rehydration of phosphophyllite and hopeite after heating has led to a preference in preparing ZPCC with a higher degree of phosphophyllite. This is because phosphophyllite remains dehydrated after heating in the application environment and does not cause the problems as seen with hopeite upon rehydration.[1] Unfortunately it is quite difficult to differentiate between the two phosphates using infrared spectroscopy and it is generally accepted that ZPCC are comprised of a mixture of the two.[9] Differentiation is made all the more difficult by the formation of coatings using tricationic baths.[8]
4.4.2 Thermal treatment of the 958+ coating

Figure 4.10: The spectra recorded of the 958+ at 120 °C, 130 °C and 140 °C.

Figure 4.10 has been prepared to show the temperature range at which the most dramatic change occurs in the infrared spectrum of the 958+ coating. At 130 °C, the intensity of the OH peak at 3564cm\(^{-1}\) begins to drop significantly. This is accompanied by a change in the shape and the wavenumber of the peak at 1640-1600cm\(^{-1}\) relating to the bending vibration of the water of hydration. This may be interpreted as dehydration of the coating due to thermal stress. The water of hydration remaining in the coating after this dehydration event is less strongly bound to the crystal lattice (through hydrogen bonding). This can be inferred from the increase in wavenumber in the broad
peak in the range 3000-3400 cm\(^{-1}\). The effect of the dehydration on the environment of the tetrahedral PO\(_4\) ions in the coating can be seen from the changes in the peaks in the region 1200-900 cm\(^{-1}\). No further changes are seen in the spectrum of the 958+ coating as the temperature increases to 150 °C.

4.4.3 Raman Spectroscopy

The Raman spectrum of the 958+ coating is shown in Figure 4.11. Signals due to scattering caused by water in the phosphate coating are significantly weaker than those found in the infrared spectra. The peak at 312.6 cm\(^{-1}\) has been identified by Pawlig et al as a reliable indicator of the presence of hopeite in a phosphate system.[7] The splitting of the PO\(_4\) \(v_3\) modes in the crystal lattice is evident in the Raman spectrum.

![Raman spectrum of the Henkel 958+ ZPCC](image-url)
The peaks at 933cm\(^{-1}\), 1065cm\(^{-1}\) and 1130cm\(^{-1}\) are thought to correspond to those in the infrared spectrum of the ZPCC that are found at 926cm\(^{-1}\), 1068cm\(^{-1}\) and 1120cm\(^{-1}\) respectively. These are the \(v_3\) modes that have become detectable as the degeneracy of the \(v_3\) is disturbed in the crystal lattice of the phosphate coating. In aqueous solution the \(v_3\) mode appears as one peak and relates to asymmetric stretching of the tetrahedral PO\(_4\) ion. The peak at 986cm\(^{-1}\) corresponds to the 995cm\(^{-1}\) peak in the infrared spectrum and results from the \(v_1\) mode of vibration of the PO\(_4\) ion. The peak at 580cm\(^{-1}\) is a result of the \(v_4\) mode and that at 310cm\(^{-1}\) is a result of the \(v_3\) mode, again of the phosphate ion.

In a Raman study on hopeite published by Sato et al, the wavenumbers for peaks associated with the hopeite crystal structure were presented. The absorptions in the range 900-1150cm\(^{-1}\) differ slightly, yet consistently from those recorded for the 958+ coating. This may indicate the presence of phosphophyllite in the composition of the coating.
4.4.4 Thermal treatment of the 958+ coating

The Raman spectrum of the thermally treated 958+ coating is shown in Figure 4.12.

The most significant change in the spectrum occurs with the blue shift of the peak at 933cm\textsuperscript{-1} to a value of 946cm\textsuperscript{-1}. The peak at 303cm\textsuperscript{-1} results from a 7cm\textsuperscript{-1} redshift of the $v_3$ PO\textsubscript{4} peak. The peak shift at 607cm\textsuperscript{-1} from 580cm\textsuperscript{-1} of the $v_4$ is also large. The change in the asymmetric stretch, $v_3$ scattering energies may be interpreted as resulting from the dehydration of the ZPCC coating induced by the thermal stress. The loss of water hydration will change the crystal structure of the coating therefore changing the effect the crystal structure has on the degeneracy of the asymmetric stretch modes of the phosphate ion.

Figure 4.12: Raman spectrum of the thermally treated Henkel 958+ ZPCC
4.4.5 Elemental Dispersive X-ray Analysis (EDX)

The EDX spectrum of the Henkel 958 + ZPCC is shown in Figure 4.13. The spectrum was recorded at an accelerating voltage of 20kV in an effort to detect any Zr species at the surface resulting from the deoxylate rinse. It may be concluded that a tricationic bath was used to prepare the ZPCC as both Ni and Mn are detected in the spectrum as well as Zn. At such a high accelerating voltage it is assumed that the Fe signal is being detected from the substrate as well as any that may be incorporated in the coating.
The EDX maps of the surface are not included here as they do not produce any readily observable qualitative information.

Figure 4.14 is the sum spectrum of the Henkel 958+ ZPCC after having being thermally treated in a manner analogous to the prebake step of the injection moulding rubber to metal bonding process.

Unfortunately, given that the surface of the 958+ coating is of an irregular morphology, no quantitative analysis can be performed whereby the pre and post heating spectra can be compared. However it was seen that there is a significantly more intense peak for oxygen in the spectrum of the post heating sample. The oxygen detected after heating must be incorporated from the ambient atmosphere of the coating during the heating process. The 958+ coating has been shown to lose water of hydration during heating using infrared spectroscopy. This would be expected to yield a simultaneous loss of oxygen content in the coating. However this is not apparent from the EDX analysis. Oxidation of the metallic species in the coating or at the substrate may be occurring. The porosity of the coating will not protect the substrate from this reaction.[10] It is unknown at this stage whether the dehydration process plays any role in this putative oxidation process.
Figure 4.14: Sum spectrum of the Henkel 958+ ZPCC after thermal treatment
4.5 Conclusions

4.5.1 The interaction of the GM and the Mild Steel Substrate

XPS results indicate that the GM condensate deposits at the MPMSL. However the amount of the GM deposited is not enough to completely cover the substrate surface. Also, visual inspection alone indicates that the GM deposit must be in the region of a few monolayers as there is no visible difference to the surface before or after the heat treatment with the GM. This fact is further emphasised by the inability of the Anasys technicians to record a satisfactory spectrum from the heat treated GM-MPMSS surface.

4.5.2 Complex Substrates: Zinc Phosphate Conversion Coating on Mild Steel

The analysis of the Henkel 958+ ZPCC has revealed that the coating dehydrates during thermal stress. There is oxidation of either the Fe substrate or metallic inclusions from the phosphating bath caused by thermal stress. It is expected that the GM will be hydrolysed more fully by a substrate that stores water as a result of its preparation and releases this water as it is heated. Unfortunately, the impact of the ZPCC dehydration on the hydrolysis and condensation of the GM was not recorded. It must be noted however that the GM alkoxysilane moiety is not the only part of the GM molecule that will interact with the ZPCC. It has been reported that coordination complexes of \( N, N\)-dimethyl-4-dinitrosoaniline (pDMNA) and \( \text{ZnCl}_2 \) are easily prepared. The coordination complex is believed to be formed through the interaction of the zinc ion with the non-bonding electron pair on the nitroso nitrogen atom.[11]

\[
\begin{array}{c c c}
\text{O} & \text{N} & \text{R} \\
\text{O} & \text{N} & \text{R} \\
\text{Zn}^{2+} & & \\
\end{array}
\]

Scheme 9: Coordination between the GM nitroso moiety and the zinc cation.
A coordination complex of the GM and ZnCl₂ was also prepared during the project thus confirming that the affinity of the nitroso functional group in the GM was comparable to that of the pDMNA. The coordination complex was red in colour. The alkoxyisilane moiety of the GM also appeared to react with the zinc salt and the product was determined to be highly condensed by the zinc salt. Therefore a very complex interaction between the GM and a given ZPCC is expected.
4.6 References


5 Chapter 5: Analysis of the GM Nitroso Reactivity

5.1 Introduction

5.1.1 Solution NMR Results for the GM Nitroso Reaction with Ene Substrates

The results relating to the GM nitroso reactivity in solution are presented and the ene reactivity of the GM nitroso moiety has been outlined in Chapter 1, section 7. In order to investigate this process, an analogue of the GM nitroso moiety was chosen as well as a simple ene substrate. This was done in order to provide a simplified assessment of the reaction before moving on to the more complex interaction that is expected between the multi-functional GM and the NR analogue cis-1, 4-polyisoprene (C14PI).

\(\text{\textit{N, N-dimethyl-4-nitrosoaniline (pDMNA) was chosen to act as the GM nitroso analogue and 1-methyl-1-cyclohexene (1M1C) was chosen to act as ene substrate. The reaction of pDMNA with C14PI was also examined (Figure 5.1).}}\)

\[
\text{A} \quad \text{B} \quad \text{C}
\]

\(\text{Figure 5.1: 1-methyl-1-cyclohexene (A), } \text{N, N-dimethyl-4-nitrosoaniline (B) and } \text{cis-1, 4-polyisoprene (C).}\)

In an effort to study the interaction between the enophile and ene substrate in any given reaction, the NMR spectra of the reactants were recorded as a function of temperature in a high boiling point solvent such as DMSO-d6 or Toluene-d8. This process was not successful when the solvent used was toluene, the NMR spectrometer failed to lock
correctly in these instances. In the other reactions, spectra of the reaction mixture were recorded before and after execution of the reaction *in-situ* in the NMR tube. The results are presented in section 5.3.

### 5.1.2 GM Nitroso Reaction with NR in the Application Environment

The reactivity of the GM with NR was examined by preparing mirror polished mild steel screw (MPMSS) substrates, coating them with the GM in isolation and subjecting these parts to the injection moulding process with NR. The results are presented in section 5.4.

### 5.2 Experimental

#### 5.2.1 Section 5.3: Sample Preparation

<table>
<thead>
<tr>
<th>Section</th>
<th>Enophile</th>
<th>Ene</th>
<th>Enophile Mass (g)</th>
<th>Ene Mass (g)</th>
<th>Solvent</th>
<th>Solvent Mass (g)</th>
<th>Total Reactant Concentration (wt%)</th>
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<td>1M1C</td>
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<td>0.15</td>
<td>Tol-d8</td>
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<td>C14PI</td>
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<td>Tol-d8</td>
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Table 5-1: Masses and reactants used in NMR experiments in section 5.3.

#### 5.2.2 Section 5.3: Overnight Reaction of pDMNA and 1M1C

1.139g of 1M1C was reacted with 0.095g of pDMNA in 15ml of anhydrous toluene at 100 °C. The reaction was allowed to run overnight and the solvent and unreacted 1M1C
were removed in vacuo prior to NMR analysis. The NMR sample was prepared in Toluene-d8.

5.2.3 Section 5.4: MPMSS-GM-NR Injection Moulded Samples

The samples for MPMSS-GM-NR injection moulding experiments were prepared as follows. Mild steel screws with a 1” diameter circular face were grinded with Streurs SiC foil backed grinding paper. The grinding was carried out using decreasing grit size, starting with 120 grain, 500 grain, 800 grain and finishing with 1200 grain. The screws were sonicated in hexane for fifteen minutes in between each step to remove contamination. The grinding was followed by polishing using 9µm, 3µm & 1µm diamond suspension: Struers DiaDuo. The polishing was carried out using Streurs MD Nap polishing pads, magnetically fixed to the polishing wheel. Separate pads were used for each grade of diamond suspension and the pieces were cleaned thoroughly using sonication in hexane in between polishing steps. The MPMSS samples were spray coated with a GM/EtOAc solution of 8wt% concentration at the Henkel laboratory. The spray coated samples were allowed to dry in ambient atmosphere for at least 1hr. The screws were mounted on a die for injection moulding. The die had a capacity for holding 16 screws therefore allowing for the preparation of 8 buffers per run. Two buffers comprising the cured natural rubber and 4 of the MPMSS-GM screws were prepared.

Injection Moulding was carried out on site at the Henkel laboratory in Whitestown, Tallaght. The rubber used for the preparation of the buffers was Gumasolv NR60, the composition of which is presented in Table 5-2. The unvulcanised rubber was cut into small parts and fed into the extruder of the injection moulding device. The rubber was heated to a temperature of 70 °C during the extrusion process. The GM coated MPMSS were brought to the temperature of the curing process and allowed to prebake for 5
minutes. The temperatures used were 120 °C, 140 °C and 160 °C. The curing time at each temperature was 1hr, 20 minutes and 5 minutes respectively. The change in the length of the curing time was determined using a rheometer on site.

<table>
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<tr>
<th>Raw Material</th>
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<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Rubber TSR 10 CV</td>
<td>100</td>
<td>ML 1+4/100 °C =53±4ME</td>
</tr>
<tr>
<td>Carbon Black N772</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>Processing Auxiliary B</td>
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<td>e.g. Aktiplast M</td>
</tr>
<tr>
<td>TMQ</td>
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<td></td>
</tr>
<tr>
<td>6PPD</td>
<td>2</td>
<td></td>
</tr>
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<td>Paraffin Wax Type A</td>
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<td>Solidifying point 57-62 °C</td>
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<td></td>
</tr>
<tr>
<td>Zinc Oxide</td>
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<td></td>
</tr>
<tr>
<td>Sulphur</td>
<td>4</td>
<td>Max 5% Oil</td>
</tr>
<tr>
<td>CBS</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>165.6</td>
<td></td>
</tr>
</tbody>
</table>

Table 5-2: The composition of the rubber used in sample buffer preparation.

5.2.4 Materials and Equipment

1-methyl-1-cyclohexene, \( N,N\)-Dimethyl-4-nitrosoaniline, cis-1,4-polyisoprene, toluene d8 supplied by Sigma-Aldrich Ireland Limited, Vale Road, Arklow, Wicklow, Ireland.


Mild steel screws, Unvulcanised natural rubber Gumasolv NR60 and 8wt% GM/EtOAc solution supplied by Henkel: Henkel Ireland Ltd.(RD&E), Tallaght Business Park, Whitestown, Tallaght, Dublin 24.
Metallurgical supplies were sourced form Mason Technology, 228 S Circular Rd, Merchants Quay, Dublin.

5.3 NMR Spectroscopy of Nitroso Ene Reactivity

5.3.1 The reaction of pDMNA with 1M1C

A reaction between pDMNA and excess 1M1C was carried out in toluene-d8. The proton NMR of the reaction mixture was recorded before and after heating of the reagents. The region selected for presentation in Figure 5.2 was chosen in order to highlight the formation of a nitro product, the aromatic proton peaks for which are detected at 8.016ppm (I) and (II) 5.981ppm. The identity of the product was determined by carrying out a reaction of pDMNA and 1M1C in dry toluene to increase the concentration of the nitro product and recording the LCMS spectra associated with the

Figure 5.2: The 5.8-8.2ppm region of the NMR spectra recorded for 1M1C and pDMNA before (A) and after (B) heating to 100 °C.
products. The $^1$H NMR spectrum of the concentrated product is shown in Figure 5.4. Proton correlation spectroscopy (COSY) confirmed that these peaks are related to one another (Figure 5.5). LCMS results indicated that the major product from the reaction mixture was a nitroaniline derivative of pDMNA with a molecular ion at 167m/z (Figure 5.6). LCMS results also indicated that the reaction had not gone to completion as there was still a large peak for the pDMNA reactant.

![Structure](image)

Figure 5.3: Structure of the nitro derivative of pDMNA, $N, N$ – dimethyl – 4-nitroaniline ($C_8H_{10}N_2O_2$; 166.18 g/mol).
Figure 5.4: The 5-9ppm region of the proton spectrum of the pDMNA/1M1C reaction mixture. The nitro aromatic proton peaks are indicated at 8.042ppm (I) and 5.962ppm (II).
Figure 5.5: COSY 2D correlated spectrum of the nitro product showing the coupling of the nitro aromatic protons indicated at 8.042ppm and 5.962ppm.

Figure 5.6: LCMS spectrum of the nitro reaction product from the pDMNA/1M1C reaction. The molecular ion of the nitro product is detected at 167.1m/z.
5.3.2 The reaction of pDMNA with C14PI

Figure 5.7: The 5.8-8.4ppm region of the 1H spectra of the pDMNA/C14PI reaction mixture before (A) and after (B) heating.

Figure 5.7 shows that the nitro aromatic proton peaks are detected for the pDMNA/C14PI reaction mixture after heating at 8.014ppm (I) and 5.982ppm (II). This is consistent with the nitro formation observed for the interaction of the pDMNA with the 1M1C.
5.3.3 The reaction of GM with 1M1C

NMR spectra were recorded as a function of temperature.

Figure 5.8 shows the formation of the down-field nitro aromatic proton peak at 8.033ppm (*) as the sample is maintained at 100 °C for approximately 50 minutes. The peaks for the protons para to the protons shown in Figure 5.8 were obscured by overlapping peaks.
5.3.4 The reaction of GM with C14PI

Figure 5.9: The 5.8-9ppm region of the GM/C14PI reaction mixture proton NMR before (A) and (B) after heating.

Figure 5.9 shows the nitro proton peaks at 8.019ppm (I) and 6.198ppm (II) for the GM/C14PI reaction.

5.4 Infrared Spectroscopy: The GM in the Application Environment

5.4.1 Interaction of the GM with NR: Injection Moulding and Curing

Mirror polished mild steel screws (MPMSS) were coated with the GM and subjected to the process of injection moulding at the Henkel laboratory. The mirror polishing of the screws was bound to prevent the formation of a satisfactory bond with the rubber injected into the die. However, small quantities of rubber remained fixed to MPMSS surfaces after they were separated from the vulcanizate. From these samples it was possible to identify how the GM performed during the experiment.
Figure 5.10: On the left, low (x2.5 metallurgical objective) and high magnification (FTIR microscope) of the NR surface after injection moulding. On the right, the MPMSS surface is shown. The vertical edge of the FTIR microscope image is approximately 200µm.

Figure 5.10 shows the surfaces of the vulcanizate and the MPMSS after injection moulding. On the MPMSS side, the remaining rubber is bonded to a coloured residue which in turn is bonded to the MPMSS surface. A clear fracture edge can be seen on the rubber attached to the MPMSS, the mirror image of which is easily discernible on the NR vulcanizate surface on the left (Figure 5.10 A). The principle finding from the analysis of this fracture site is that the rubber has been modified by the GM during curing. An FTIR spectrum taken from the surface of the fracture site at the vulcanizate side (Figure 5.10 A) is shown in Figure 5.11 along with that of the GM at 160 ° C.
Figure 5.11: (a) The spectrum of the surface of the GM modified vulcanized rubber at the fracture site located on the rubber surface and (b) The spectrum of the GM at 160 °C.

The spectra share enough significant peaks to indicate that the GM is present in the NR matrix at the cured rubber substrate surface. These peaks include:

- (I): the urethane secondary amine stretch absorption at ca. 3300 cm$^{-1}$
- (II): the C-H stretch vibrations of the GM as well as those of the NR in (a)
- (III): the strong carbonyl absorption peak at 1706 cm$^{-1}$ in (a) and 1726 cm$^{-1}$ in (b)
- (IV): the symmetric stretch of the double bonds in the aromatic ring at 1600 cm$^{-1}$ in both (a) and (b)
Comparison of the carbonyl absorption frequency in spectrums (a) and (b) may be interpreted as follows. The GM at 160 °C may be considered to be mostly composed of free monomers that are not engaged in hydrogen bonding. This results in the high frequency of the carbonyl absorption of the GM at 160 °C (1726 cm$^{-1}$). Comparison of the wavenumber of the carbonyl absorption of the GM at 160 °C and that of the GM modified NR (1706 cm$^{-1}$) shows that there is 20 cm$^{-1}$ difference in the frequency of absorption. From this it may be concluded then that the GM modified NR is engaged in dimeric hydrogen bonding. [1]

There is an indication that the nitroso content of the GM detected at the vulcanizate surface has changed during the injection moulding process. From the work of Gowenlock et al., the nitroso group of a para dialkylamino nitrosoaniline absorbs at ca. 1380 cm$^{-1}$. [2], [3]

In Figure 5.11, there is a significant decrease in the absorption at 1389 cm$^{-1}$ in the spectrum of the GM modified NR when compared to the spectrum of the thermally treated GM. While this indicates that the nitroso functional group is consumed during the interaction with the GM, there is no indication if this has led to the formation of a covalent bond between the GM and the NR. It is possible that the nitroso moiety has reacted with some other ingredient in the NR formulation and the GM modified NR is a mixture of this reaction product and the NR.

The sites at which the GM modified NR was detected are indicated in Figure 5.12. The dark deposit indicated by label ‘A’ showed a very strong IR signal for the GM as well as the NR. Site B at the perimeter of the GM modified NR showed a very weak band associated with the GM. Site C showed no indication of the GM in the IR spectrum.
Figure 5.12: The NR vulcanizate surface after injection moulding. (A) Strong overlapping GM and NR FTIR signal, (B) Strong NR, weak GM NR signal and (C) NR FTIR signal, no GM detected.

5.4.2 Interaction of the GM modified NR with the MPMSS Substrate: Injection Moulding and Curing

The modification of the NR by the GM reported in the previous section has not included the results relating to the residue visible in Figure 5.10 on the MPMSS surface associated with the GM modified NR deposit. It is necessary to present the results associated with this residue in a separate section as they relate to a complex interaction between the GM modified NR and the MPMSS surface during the injection moulding and curing process.
Figure 5.13: Image taken using the FTIR microscope. The residue remaining between the GM modified rubber and the MPMSS surface after injection moulding and curing at 160 °C. The vertical edge of this image is approximately 200µm.

This residue is shown in Figure 5.13. The colour of the residue varies from green/blue to red. EDX analysis of the residue (Figure 5.14) indicates that this residue is a sulphate formed during the injection moulding/curing process.
Figure 5.14: Elemental mapping of the residue indicated in Figure 5.13. Clockwise from top left; the electron image of the residue; the O Kα map; the Fe Lα map and the S Kα map. The overlap of S and O signals is clear. The coverage of the mild steel substrate is indicated by the dark areas in the Fe X-ray signal. The image and mapping was carried out at x1.1K magnification.
The IR spectrum of the residue is shown in Figure 5.15. The residue bears none of the distinguishing absorption peaks that are associated with the IR fingerprint of the GM in the region 1450-1750 cm\(^{-1}\). The principle characteristic absorption peaks of the residue occur at 856 cm\(^{-1}\), 1218 cm\(^{-1}\) and 3262 cm\(^{-1}\). Absorption at these wavenumbers is typical of metal sulphate compounds.[4] Two peaks at 2927 cm\(^{-1}\) and 2857 cm\(^{-1}\) indicate that there is rubber present in the residue also.

Figure 5.16 shows an image taken from the MPMSS surface of an adhesion sample that was prepared at 140 °C. The sulphate residue is seen here in a droplet formation at the edge of the GM modified NR. From this image it appears that the elemental sulphur of
the vulcanizate is released from the NR during the curing process which proceeds at high temperature and pressure.

Figure 5.16: The ‘droplet’ like features observed on the 140 °C adhesion sample. The vertical edge of this image is approximately 200μm.

In Figure 5.17, a regular and patterned feature was observed at GM/NR deposits at the MPMSS surface after injection moulding and curing at 120 °C. The ‘star’ like defects were found at sites where a mixture of the sulphate residue and the NR were detected.
Figure 5.17: The star-like features detected at the MPMSS surface in areas where the sulphate residue-MPMSS mixture was detected. These features were found on the surface of MPMSS that was subjected to 120 °C during injection moulding and curing.

The MPMSS surface in this image has been ‘bleached’ by the intensity of the illumination required to record an image of the feature of satisfactory resolution. The vertical edge of this image is approximately 200µm.
Figure 5.18: x50 magnification image taken of sulphate crystals remaining on the GM modified NR surface. The dimensions of the sulphate crystals are indicated.

The sulphate ‘stars’ that separated from the MPMSS sulphate residue remained on the GM modified rubber surface of the cured rubber buffer.

The EDX elemental maps of a site from the image in Figure 5.17 are shown in Figure 5.19. The exposure of the mild steel substrate as indicated by the Fe Lα map show that the sulphate residue is not present and may have been removed by the NR on separating or did not deposit at the site at any stage.
Figure 5.19: The elemental maps recorded using EDX of the star-like features in Figure 5.17. Clockwise from top left; the electron image of the residue; the O Kα map; the Fe Lα map and the S Kα map. The image and mapping was carried out at x900 magnification.

A final aspect of the sulphate formation is presented in Figure 5.20. The structure of the sulphate changes as the curing temperature of the piece increases. In the 120 °C oxygen elemental map, the structure of the sulphate is crystalline in the areas where it is clearly discerned. In the 140 °C map, an area where a mixture of the crystalline sulphate and amorphous sulphate are present together is shown. In the 160 °C, the amorphous sulphate is shown. No crystalline sulphate was detected at the surface of the 160 °C cure sample.
Figure 5.20: Oxygen elemental maps recorded using SEM/EDX for the sulphate formed at the MPMSS surface. The prebake and curing temperature for each sample is 120 °C (top), 140 °C (middle) and 160 °C (bottom). The magnification is x900, x1.1k and 1.1k respectively.
5.5 Conclusions

5.5.1 Solution NMR Results for the GM Nitroso Reaction with Ene Substrates

The principle finding from the investigation of the reactivity of the GM nitroso moiety and ene substrates is that the nitroso functional group will convert to a nitro group in conditions where it is heated in the presence of both an ene substrate and oxygen. This aspect of the reactivity of nitrosoanilines and olefins was commented on in a paper published by Cain et al.[5] This paper, dealing with the preparation and reaction of rubber bound antioxidants, stated that the drawbacks of preparing \( p \)-phenylenediamines from nitrosoaniline and olefin starting products were that the olefin concentration was required to be in a large excess and that no oxygen was present when carrying out the reaction. As is seen from the reactions carried out in this body of work, the presence of oxygen results in the conversion of the nitroso group to a nitro group in the presence of the ene substrate. In Chapter 3, no such conversion was detected in samples where the GM was heated to the application temperature; the nitroso functional group remained unchanged after heating.

In the context of the project, this rules out the inclusion of ene substrates in the formulation if it is to be prebaked in ambient atmosphere prior to the injection moulding of the NR. In section 5.4 it was shown that the GM mixes with the NR during the injection moulding process. The IR data shows that there is a change in the spectrum of the GM in the NR/GM mixture that indicates that the GM nitroso group has been consumed during this process. Unfortunately, there is no indication from the IR results that either the amine link that is desired of the NR GM interaction is formed, or the nitro group that has been shown to consistently be generated in the reactions presented in this chapter.
5.5.2 Infrared Spectroscopy: The GM in the Application Environment

The results from the injection moulded samples indicate a complex interaction between the GM and the NR in the application environment. There are two key aspects to the GM-NR interaction.

Firstly, it has been shown that the GM mixes with the NR during the injection moulding process. The GM modified NR that results may or may not be covalently bonded together however it has been shown that the nitroso moiety has reacted to some extent during the mixing process with the GM. This GM modified NR appears to be absorbed into the body of the NR as only a small amount comprises the surface area of the NR vulcanizate that was in contact with the MPMSS surface.

Secondly, the NR modified by the GM expels vulcanizing sulphur additives during the injection moulding/curing process. Sulphate deposits were only detected in the vicinity of GM modified NR deposits on the MPMSS surface indicating that this was not a general reaction occurring between the NR and the MPMSS surface. The structure of the sulphate detected at the surface was temperature dependent: higher temperature curing favouring the formation of amorphous sulphates, lower temperature curing producing crystalline deposits.

In order to translate what these observations imply collectively about the interaction of the GM and the NR in the application environment on the MPMSS surface, it is necessary to present the following diagrams.
Figure 5.21: A schematic of the GM-NR disbonded part after injection moulding. (A) The NR vulcanize, (B) the GM modified NR remaining at the NR side of the part, the GM modified NR remaining at the MPMSS side (C), (D) the sulphate released at the MPMSS surface by the GM modified NR and (E) the MPMSS substrate.

This shows the injection moulded piece after removal from the buffer die. Prior to the injection moulding process, the MPMSS surface is coated with the GM. When the GM at the MPMSS surface meets the GM it mixes and there are two possible ways in which this happens. These are presented in Figure 5.22 and Figure 5.23.
Figure 5.22: The first proposed mechanism for the behaviour of the GM-NR-MPMSS system in the injection moulding and curing environment.

(A) The GM Layer and the NR are in contact at the outset of injection moulding: they mix and react to form the GM modified NR.

(B) The GM modified NR layer cures at a different rate to the NR in its vicinity and this begins to draw it together and into the body of the curing NR.

(C) The GM modified NR layer reacts and releases sulphur compounds from the NR on to the MPMSS surface.

(D) The sulphate layer is formed at the site where the GM modified NR is in contact with the MPMSS.
Figure 5.23: The second proposed mechanism for the behaviour of the GM-NR-PMMSS system in the injection moulding and curing environment.

(A) The GM Layer and the NR are in contact at the outset of injection moulding: the GM layer is immediately drawn into the body of the NR.

(B) The GM mixes and reacts with the NR. Simultaneously, the elemental sulphur in the NR are deposited on to the MPMSS surface.

(C) The sulphate layer is formed at the site where the GM modified NR is in contact with the MPMSS.

Of these two mechanisms, the likeliest appears to be the second. The high pressure conditions at which the NR is introduced to the substrate would suffice to cause the absorption of the GM into the body of the NR. The subsequent reaction of the GM and the NR is then responsible for the release of sulphur based compounds form the NR which in turn form sulphate deposits at the MPMSS surface. The ejection of sulphur
from the NR during the interaction of the GM and the NR indicates that the reaction between the rubber and the coupling agent happens more rapidly than that between the NR and the elemental sulphur.

5.6 References


Chapter 6: Adhesion Testing; Impact of Prebake/Cure Temperature on Adhesion performance

6.1 Introduction

The manner in which thermal stress affects the chemical structure of the GM was initially indicated by the findings from the in-situ vibrational analysis of the GM on a mirror polished mild steel substrate in Chapter 3. In order to determine how the GM affects the industrial formulation in which it is included when subjected to thermal stress the following experiment was designed:

(a) Three sample sets consisting of the formulation spray coated on to grit blasted mild steel screws (GBMSS) were prepared.

(b) Each sample set was then used to prepare rubber to metal bonded parts at different prebake/curing temperatures via the injection moulding process.

(c) The tensile strength of the rubber to metal bonded parts was then tested.

(d) SEM/EDX analysis of the bonds after adhesion testing was carried out.

The aim of the experiment was to investigate the impact of the condensation state of the GM on the formulation performance. From the vibrational analysis of the GM as thin films on mild steel, it was seen that the GM hydrolyses and condenses as the temperature of its environment increases. Similarly, the NMR analysis of the GM shows that the GM hydrolyses and condenses at the application temperature. By adjusting the temperature at which the GM formulation is used to bond rubber to metal, the impact of the state of the GM at a given bonding temperature may be analysed. The results are presented in the following sections.
6.2 Experimental

6.2.1 Section 6.3: Sample Preparation

Mild steel screws were grit blasted on site at the Henkel laboratory. After grit blasting, the screws were washed with isopropanol. The screws were then coated with the Henkel formulation containing the GM designated the R2M, batch no. 13-1#. After coating, the samples were left to sit for an hour to allow evaporation of the carrier solvents. The surface of the screws used in the experiment was corrugated and as a result, the thickness of the coatings varied from the peaks and troughs of the surface features (Figure 6.1).

![Figure 6.1: Peaks and troughs from the surface corrugation of the mild steel screws used in the adhesion experiment.](image)

The general trends in the thickness resulting from the surface features of the mild steel screws are indicated in Figure 6.2.
The formulation coated screws were then subjected to the injection moulding/curing process which has been outlined in Chapter 5, section 5.2.3.

Figure 6.2: (a) Cross section of the peak feature on the mild steel screw surface. The thickness decreases to ca. 1µm at the top of the peak. (b) Cross section of the trough feature: the thickness of the formulation in the trough was found to approach a maximum of ca. 20µm.
6.2.2 Section 6.3: Tensile Strength Testing

Tensile strength testing was carried out on site by the staff in the Henkel laboratory, Whitestown Industrial Estate, Tallaght. The samples were tested using an Instron 5500R materials testing system and results were recorded using Bluehill modular applications software.

6.2.3 Section 6.3: Rubber Hardness Testing

The hardness of the cured rubber in the buffer test samples was determined using a durometer (type A) and measurements were recorded following the procedure outlined in the ASTM standard D 2240. 15 measurements were taken on cured rubber samples at each curing temperature (120 °C, 140 °C & 160 °C). The average of these measurements was reported as the representative hardness of the rubber cured at each temperature.

6.2.4 Section 6.4: Elemental Analysis of Bonds subjected to Tensile Strength Testing

Cross sections were prepared of the bond at the failure site of the tensile strength tested buffer. The mild steel screw was set in epoxy resin which was allowed to cure overnight. The grinding was carried out using decreasing grit size, starting with 120 grain, 500 grain, 800 grain and finishing with 1200 grain. A final polish using 9µm Streurs DiaDuo solution on an MD Nap polishing plate was carried out prior to preparation for the SEM/EDX analysis. Samples were coated with Carbon using the Cressington Carbon Evaporation Coater 208C. An accelerating voltage of 10kV was used for elemental analysis. Formulation coating thickness of the cured buffer samples
was seen to vary little in comparison with the samples measured and presented in Figure 6.2.

6.3 Tensile Strength Test

Table 1 shows the results for the tensile strength testing.

<table>
<thead>
<tr>
<th>Part</th>
<th>Curing Temperature (°C)</th>
<th>Tensile Stress (MPa)</th>
<th>Extension (mm)</th>
<th>Maximum Load (N)</th>
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</thead>
<tbody>
<tr>
<td>120A</td>
<td>120</td>
<td>9.348</td>
<td>63.7</td>
<td>4588</td>
</tr>
<tr>
<td>120B</td>
<td>120</td>
<td>9.181</td>
<td>63.6</td>
<td>4506</td>
</tr>
<tr>
<td>120C</td>
<td>120</td>
<td>9.704</td>
<td>64.7</td>
<td>4763</td>
</tr>
<tr>
<td>140D</td>
<td>140</td>
<td>8.947</td>
<td>59</td>
<td>4391</td>
</tr>
<tr>
<td>140E</td>
<td>140</td>
<td>8.897</td>
<td>57.9</td>
<td>4367</td>
</tr>
<tr>
<td>140F</td>
<td>140</td>
<td>9.17</td>
<td>60.1</td>
<td>4501</td>
</tr>
<tr>
<td>160G</td>
<td>160</td>
<td>7.03</td>
<td>51.5</td>
<td>3450</td>
</tr>
<tr>
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<td>160</td>
<td>5.525</td>
<td>44.3</td>
<td>2712</td>
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<td>160I</td>
<td>160</td>
<td>6.961</td>
<td>51.2</td>
<td>3416</td>
</tr>
</tbody>
</table>

Table 6-1: Adhesion testing results for the three temperature sets.

Figure 6.3 shows the tensile strength of the bonded samples. The results indicate that the tensile strength deteriorates as the prebake/curing temperature is increased. The largest decline in the tensile strength occurs when the prebake/curing temperature is increased from 140 °C to 160 °C. For each sample set, the hardness of the cured rubber
was tested at 15 sites and the average was calculated. The results of the hardness testing
are shown in Figure 6.4. The limited number of samples prepared at each
bonding/curing temperature precludes any meaningful statistical analysis of the
significance of the tensile strength testing. However, the temperature dependent nature
of oxide formation detected using SEM/EDX analysis would appear to indicate that the
poor performance of the 160 °C buffers in tensile strength testing relative the buffers
prepared at 140 °C and 120 °C is a direct result of the curing/bonding temperature. The
SEM/EDX results are presented in section 6.4.
Figure 6.3: The results from the adhesion testing carried out in the Henkel laboratory. Three buffers were prepared at each curing temperature and tested.

Figure 6.4: Average Shore hardness test results from 15 tests on rubber samples from each curing temperature
6.4 SEM EDX of Sample Cross Sections after Tensile Strength Testing

In order to identify a cause for the decrease in the Tensile strength of the adhesion joints prepared at 160 °C compared with those at 140 °C, SEM/EDX analysis was carried out on cross sections of the relevant samples. The 120 °C sample was also examined and was found to differ little to the 140 °C, therefore only the results of the 140 °C and 160 °C are presented.
Figure 6.5: SEM/EDX of the 140 °C prebake/cure cross section. The electron image recorded at x2.5k magnification and 10kV accelerating voltage (a), the sulphur elemental map (b), the carbon elemental map (c), the chlorine elemental map (d), the oxygen elemental map (e) and the iron elemental map (f).
The electron image in Figure 6.5 shows an interfacial region between the industrial formulation and the cured NR. The interface shows evidence of extension induced by the tensile strength testing. The carbon elemental map shows that there is a distinct intensity associated with the carbon content of the formulation layer and with the NR to which it is bonded. The interfacial region carbon signal exhibits a similar intensity to the cured NR. A chlorine containing compound included in the formulation overlaps at the interfacial region. It is proposed that this overlap indicates that the chlorine containing compound in the formulation and the NR provide a degree of mixing and chemical interaction that bonds the formulation and the NR. In the elemental mapping for silicon content at the bond interface, the concentration of the silicon is too low to be detected in the elemental map (Figure 6.6). Also visible in Figure 6.6 is the SiC grit embedded in the mild steel surface after grit blasting.

Figure 6.6: Comparison of the silicon content (left) and the chlorine content in the formulation layer for the 140 °C. The penetration of the chlorine into the bonding interface is greater than that of the silicon.

Oxide formation at the interface joining the formulation to the iron substrate is indicated by the oxygen elemental map. It is possible that this oxide formation is a result of alcohol released by the hydrolysis of alkoxy silane based compounds in the formulation.
It has been indicated by the Henkel staff that there is at least one other alkoxy silane other than the GM included in the formulation.

The interpretation of the sulphur elemental map must be made with caution. The intensity of the sulphur signal is similar at the cured NR, the formulation and the mild steel substrate. It is reasonable to expect that there should be no sulphur present at the mild steel substrate surface however it is possible that some cross contamination has occurred during the sample preparation which included grinding and polishing of the cross section. Although this cross contamination is not detected for other elements in the sample cross section, it may be argued that the sulphur contamination is facilitated by the inclusion of elemental sulphur in the NR formulation. There is a weak intensity increase in the sulphur signal at the mild steel-formulation interface where the oxide is detected. Above this region the sulphur signal is weaker. The sulphur signal is also weaker immediately below the interfacial region between the formulation and the NR.
Figure 6.7: SEM/EDX of the 160 °C prebake/cure cross section. The electron image recorded at x2.5k magnification and 10kV accelerating voltage (a), the sulphur elemental map (b), the carbon elemental map (c), the chlorine elemental map (d), the oxygen elemental map (e) and the iron elemental map (f).
Figure 6.7 shows the SEM/EDX results for the 160 °C prebake/cure sample. The overlap of the chlorine and the NR carbon intensities at the interfacial region is similar to that detected in the 140 °C cured samples. Also, the lack of silicon at the bonding interface has been observed (Figure 6.8).

Figure 6.8: Comparison of the silicon content (left) and the chlorine content in the formulation layer of the 160 °C sample. The penetration of the chlorine into the bonding interface is greater than that of the silicon.

The feature that distinguishes the 160 °C samples from the 140 °C samples is the thickness of the oxide layer between the formulation and the mild steel substrate. The thickness of the oxide layer in the case of the 140 °C sample was similar to that shown in Figure 6.5 in all sites examined using the SEM/EDX. This was not the case for the 160 °C sample: the oxide layer thickness was comparable to that shown in Figure 6.7 generally and it increased dramatically in some areas.

The sulphur elemental map indicates more clearly the distribution of the sulphur in the vicinity of the oxide layer of the 160 °C than in the 140 °C sample shown Figure 6.5. There is an increase in the sulphur concentration in the formulation immediately above the oxide layer. A decrease in the concentration of detected sulphur is also seen at the interfacial layer between the NR and the formulation.
6.5 Oxide Defects in the 160°C Sample

In section 7.3 the oxide layer formed between the formulation and the GMBS surface was presented. Along with this general increase in the thickness of the oxide layer, areas where the oxide formation had progressed at a significantly increased rate were also detected. A representative sample of these sites is shown in Figure 6.9.

In the electron image (Figure 6.9 (a)), it can be seen that this site at which the rubber has been removed completely by the tensile strength test. In the intervening period between tensile strength testing and sample cross section preparation, the oxide at the interface between the formulation and the GBMS surface has grown to such an extent that it has penetrated through the formulation layer. Sulphur, oxygen, iron and chlorine are detected at the oxide site. The large particles shown in the region above the formulation are believed to be remaining from the polishing and grind steps, having become embedded in the surface at the site of the oxide.
Figure 6.9: SEM/EDX of the 160 °C prebake/cure cross section. The electron image recorded at x1.2k magnification and 10kV accelerating voltage (a), the sulphur elemental map (b), the carbon elemental map (c), the chlorine elemental map (d), the oxygen elemental map (e) and the iron elemental map (f).
6.6 Conclusions

The adhesion testing of the GM containing formulation at three different sample preparation temperatures has revealed the following.

The bond between the formulation and the NR vulcanizate showed an interfacial region where the carbon signal of the NR and the chlorine signal of the formulation overlapped. Silicon was not detected in this region and sulphur was seen to be lower in concentration in the vicinity of the interface. This may provide some interesting new insight to the Henkel team as to the manner in which the NR and formulation interact during bonding.

The samples that were injection moulded and cured at 160 °C exhibited weaker bonding to the mild steel substrate than those prepared at 140 °C and 120 °C. The samples prepared at 140 °C and 120 °C had similar bond strengths. SEM/EDX analysis has indicated that there is a thicker oxide layer under the formulation in the samples prepared at 160 °C. In some places this oxide has grown rapidly and breached the formulation surface, typically in areas where the rubber was removed fully from the formulation during the tensile strength testing.

While there were significant differences observed between the samples prepared at 160 °C and those prepared at 140 °C and 120 °C, the results from this study must be regarded with caution. The injection moulding process is carried out using a complex industrial device which incorporates a NR rubber extruder, injection moulding and curing capability. Prior to the time at which the adhesion testing samples were prepared, the injection moulding equipment had been idle for at least a month. The first sample set to be prepared was the 160 °C sample set and it is possible that the sample set may have been contaminated or affected by the idle time. It is worth pointing out however,
that the NR-GM-MPMSS samples (the results for which are presented in chapter 6) did not show any signs of contamination. Nor did GBMS samples prepared with a coating of GM that were prepared in the same run at each temperature as the GBMS-Formulation samples and the NR-GM-MPMSS samples.

The formation of the oxide layer in the 160 °C sample may be a result of the complete hydrolysis of the GM in the formulation at this processing temperature. In chapter 3, it was shown that the GM hydrolyses more completely as its concentration is decreased at the application temperature of 160 °C. Given that the GM concentration in the formulation is 8 wt %, it is reasonable to expect the GM urethane hydrogen bonding is sufficiently interrupted at this concentration to facilitate the complete hydrolysis of the GM at a processing temperature of 160 °C. This hypothesis necessarily rules out any interactions between the GM and the other formulation ingredients which are unknown. If the GM has completely hydrolysed at 160 °C and is deemed to be partially hydrolysed at 140 °C and 120 °C, the amount of ethanol released by the GM is expected to be relatively higher at the higher processing temperature. It is possible that the increased amount of ethanol present at a processing temperature of 160 °C is responsible for the increase in the oxide layer formation at the formulation-mild steel interface.
Chapter 7: GM Stability in DMSO-d6

7.1 Introduction

During initial NMR experiments using the GM dissolved in DMSO-d6, it was observed that certain samples were hydrolysing relatively rapidly in the solvent. The stability of the GM in DMSO-d6 came into question and it was necessary to examine the manner in which the GM was reacting with the DMSO-d6 solvent. Literature regarding general aspects of DMSO-d6 revealed that the solvent is capable of increasing the apparent basicity of alkoxide ions in solution. [1] The increased reactivity of alkoxide ions in DMSO-d6 combined with the hygroscopic nature of the solvent was believed to be the cause of the hydrolysis that was observed. However, the effect had been exaggerated by contamination associated with a particular batch of DMSO-d6. Proton NMR spectroscopy showed that acetic acid was present at varying concentration in the ampoules of DMSO-d6 from this batch and therefore acted as the catalyst for the observed hydrolysis. The discovery that the batch of DMSO-d6 was contaminated came after a stability study had been initiated to investigate the interaction of the GM and DMSO-d6 over time. In this study, two commonly used alkoxy silane coupling agents were included to allow comparison to be drawn with the behaviour of the GM. Also, an alternative batch of DMSO-d6 which was free of the acetic acid contamination was used.

The coupling agents chosen were GPTMS ((3-glycidoxypropyl) trimethoxysilane) and MAPTMS (3-methacryloxypropyl trimethoxysilane). These were prepared at high (ca. 50 wt%) and low (ca. 10 wt%) concentrations and their hydrolysis and condensation recorded and compared with that of the GM in DMSO-d6.
7.2 Experimental

7.2.1 Sample preparation

The sample composition for the NMR stability testing of alkoxysilanes in DMSO-d6 is shown in Table 7-1. $^1$H and $^{29}$Si INEPT/RD spectra of the compounds were taken every 24 hours for two weeks and once a week for a further two weeks.

<table>
<thead>
<tr>
<th>Alkoxy silane</th>
<th>Mass (g)</th>
<th>Solvent Mass (g)</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPTMS</td>
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<td>0.661</td>
<td>43.36</td>
</tr>
<tr>
<td>MAPTMS</td>
<td>0.117</td>
<td>1.043</td>
<td>10.09</td>
</tr>
<tr>
<td>GPTMS</td>
<td>0.514</td>
<td>0.559</td>
<td>47.90</td>
</tr>
<tr>
<td>GPTMS</td>
<td>0.122</td>
<td>1.091</td>
<td>10.06</td>
</tr>
<tr>
<td>GM</td>
<td>0.592</td>
<td>0.636</td>
<td>48.21</td>
</tr>
<tr>
<td>GM</td>
<td>0.056</td>
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<td>4.62</td>
</tr>
<tr>
<td>GM</td>
<td>0.096</td>
<td>1.085</td>
<td>8.13</td>
</tr>
</tbody>
</table>

Table 7-1: The sample Composition for the NMR stability study of the GM and commonly used alkoxysilane precursors in DMSO-d6.

7.2.2 Materials and Equipment


NMR solvents supplied by: Apollo Scientific Ltd, Unit 3 & 4, Parkway, Denton, Manchester, M34 3SG, UK.

$^1$H and $^{29}$Si NMR spectra were recorded using a Bruker Avance II 400 MHz spectrometer, DIT School of Chemical and Pharmaceutical Sciences.
7.3 10.1wt% MAPTMS-DMSO-d6

7.3.1 10.1wt% MAPTMS-DMSO-d6

Figure 7.1: The $^{29}$Si INEPTRD spectra of a 10.1 wt% sample of MAPTMS DMSO-d6 as a function of time.

Figure 7.1 shows the $^{29}$Si spectra of the MAPTMS over time and the hydrolysis and condensation products that have evolved during the course of the stability study. The parent alkoxysilane peak at -42.215 ppm has been obscured to allow for clearer representation of the reaction products by expansion of the spectra baseline in the overlay. The peak labelled ‘I’ at -41.908ppm is that of the silanol: the hydrolysis products for the MAPTMS are uncomplicated in comparison to those of the GM seen in chapter 3. The peak labelled -50.59ppm is that of the $T^1$ condensate. Peak ‘III’ is a very weak signal at -59.473ppm relating to the $T^2$ condensate.
7.3.2 43.4wt% MAPTMS-DMSO-d6

Figure 7.2: The $^{29}$Si INEPTRD spectra of a 43.4 wt% sample of MAPTMS DMSO-d6 as a function of time.

The peaks labelled ‘I’, ‘II’ and ‘III’ in Figure 7.2 are found at -42.064ppm, -50.706ppm and -59.49ppm respectively. The rate of hydrolysis and condensation is higher than that of the 10wt% sample as expected. The peak for the T$_1$ condensate appears in the initial spectrum. The T$_2$ peak is appears at the 96hr point of the study. The behaviour of the silanol peak at -42.64ppm is different to that of the 10wt%. The intensity of the peak increases to a maximum at around 48hrs and diminishes to close to zero at the 552hr point. The silanols initially produced are consumed by the condensation reactions. The increased concentration of the MAPTMS precursor in the DMSO has led to more rapid and extensive hydrolysis and condensation of the MAPTMS precursor in the DMSO solution than the sample prepared at lower concentration.
7.3.3 10.1 wt% GPTMS-DMSO-d6

![Figure 7.3: The $^{29}$Si INEPTRD spectra of a 10.1 wt% sample of GPTMS DMSO-d6 as a function of time.](image)

The GPTMS alkoxy silane coupling agent proved to be relatively less susceptible to hydrolysis and condensation than the MAPTMS at both concentrations examined. Silanol peaks (labelled here as ‘I’ and ‘II’ at -41.39ppm and -41.9ppm) are the dominant reaction product from the interaction of the GPTMS with the DMSO-d6. A very weak peak at -50.742ppm (III) appearing at the 552hr point of the analysis is related to the T$^1$ condensate of the GPTMS.
7.3.4 47.9 wt% GPTMS-DMSO-d6

Figure 7.4: The $^{29}$Si INEPTRD spectra of a 47.9 wt% sample of GPTMS DMSO-d6 as a function of time.

Similar to the case of the high concentration MAPTMS sample, a peak relating to $T^1$ condensates at -50.31 ppm (III) was detected in the initial spectrum of the concentrated GPTMS sample. A single silanol peak at -41.46 ppm (I), indicating the onset of hydrolysis from the 48hr point onward, was detected in contrast to the two observed in the 10wt% spectra. The $T^1$ peak increases in intensity and complexity as the condensation reactions proceed. The $T^2$ peak at -59.146 ppm (IV) was detected for the 552hr spectrum. Over all, the reaction products produced weak peaks when compared to the 43.4 wt% MAPTMS sample. This implies that the MAPTMS is more susceptible to hydrolysis and condensation reactions in DMSO-d6 than the GPTMS.
7.3.5 8.1wt% GM-DMSO-d6

Figure 7.5: The $^{29}$Si INEPTRD spectra of an 8.1wt% sample of GM in DMSO-d6 as a function of time.

After 552 hr the only change in the spectrum of the GM 8.1wt% sample is the appearance of a very weak silanol peak at -43.89pm (I). The GM is stable in the DMSO-d6 relative to the GPTMS and MAPTMS samples at the 10.1wt%.
7.3.6 48.2wt% GM-DMSO-d6

Figure 7.6: The $^{29}$Si INEPTRD spectra of a 48.2wt% sample of GM in DMSO-d6 as a function of time.

The onset of hydrolysis at 192hr is indicated by the silanol peak at -43.86ppm (I). The GM sample follows the same trends as the GPTMS and MAPTMS at high concentration. Hydrolysis begins earlier in the high concentration sample in relation in comparison with the low concentration sample as expected.
7.4 Conclusions

The GM exhibits excellent stability in challenging chemical environments. This stability is ascribed to the hydrogen bonding between the urethane secondary amine and carbonyl sites on the molecule. It is proposed that this interaction sterically hinders the formation of the pentacoordinate intermediate that plays a role in the hydrolysis reactions of alkoxy silanes. The stability provided by urethane hydrogen bonding is one that may be capitalised upon in the wider context of alkoxy silane coupling agents in industry as surface modifying treatments. It is common in industry to apply washes containing organofunctional alkoxy silanes to inorganic surfaces as a processing step. As outlined in Chapter 1, hydrolysis and condensation of organofunctional alkoxy silanes is a challenging and complex chemical process that sees many different concurrent reactions proceeding at a variety of rates. These processes are also very sensitive to reaction conditions such as the choice of catalyst and the ratio of aqueous and non-aqueous solvent in the reaction mixture. It is proposed that the stability provided by the incorporation of the urethane moiety can be introduced into this type of surface processing and provide improved compounds for the modification of surfaces in industrial processes.
Scheme 10: Reaction of 2-hydroxyethyl methacrylate with (3-isocyanatopropyl) triethoxysilane. The product is a urethane modified MAPTMS for application in surface treatment washes.

For instance, by reacting 2-hydroxyethyl methacrylate with (3-isocyanatopropyl) triethoxysilane, a new surface modifying reagent is prepared that incorporates the urethane group and takes advantage of its impact on the reactivity of the alkoxysilane (Scheme 1). The same applies to any other organofunctionality commonly used in alkoxysilane surface treatments.

7.5 References

Chapter 8: Conclusions and Future Work

8.1 Introduction

In chapter 1 the following research questions were outlined:

- To identify any intramolecular or intermolecular changes induced in the GM by thermal stress. (Ch. 3)
- To investigate how the GM interacts with a mild steel substrate and also with more complex substrates. (Ch. 4)
- To investigate the reactivity of the nitroso moiety of the GM with the primary component of the NR, the cis-1, 4-polyisoprene. (Ch. 5)
- To examine the effect of thermal stress on the rubber-to-metal formulation containing the GM. (Ch. 6)

The conclusions for each section will be structured around the themes in each question. A fifth section has been added to highlight the potential opportunities that may be realised by applying the GM synthesis to prepare other organofunctional alkoxysilanes.

Following the conclusions there is a presentation of the future work that could potentially be carried out based on the findings from this project.
8.2 The intramolecular or intermolecular changes induced in the GM by thermal stress.

8.2.1 Vibrational analysis:

Infrared analysis revealed that the GM is engaged in hydrogen bonding via the urethane moiety. The secondary amine and the carbonyl of the urethane facilitate this association and it results in three different intermolecular states for the GM:

- The GM is a crystalline solid and polymeric hydrogen bonding is detected (a)
- At ca. 65 °C the GM melts and in its liquid state it is found to exist as an equilibrium associated dimers and free monomers (b)
- The concentration of monomers increases with temperature (c).

![Figure 8.1: Schematic of the intermolecular changes that occur in the GM as temperature increases.](image)

As temperature increases and the intermolecular state of the GM changes, it also undergoes hydrolysis and condensation. Disiloxane, a T1 condensation product, was detected using Raman spectroscopy. It was seen to have a temperature dependent
concentration reaching a peak concentration at ca. 130 °C, after which the peak intensity declined sharply reaching a negligible intensity at the application temperature 160 °C. Thermogravimmetric analysis data supported this with rapid degradation occurring from 140°C onwards.

8.2.2 NMR analysis:

The vibrational analysis was carried out on pure films of the GM in a model of the application environment. Solution NMR spectroscopy revealed the role that the concentration plays in the dynamic intermolecular and intramolecular processes identified above.

![Diagram](image)

Figure 8.2: The concentration dependence of dimers and monomers of the GM in solution. (a) At low concentrations the monomers outnumber the dimers. (b) As the concentration increases, dimerization of the GM increases.

It must be remembered that hydrogen bonded urethane compounds exist in an equilibrium between associated and free molecules: the concentration of the former decreases with the overall concentration of the compound in solution. Therefore, it is useful to interpret the reactivity of a given sample in terms of its concentration.

- The thermal reactivity of a concentrated (ca. 50wt%) sample may be regarded as being directed by the contribution of the hydrogen bonded dimers.
• The thermal reactivity of a dilute (ca. 5wt%) sample may be regarded as being directed by the contribution of the unassociated monomer.

It is more practical to present the solution reactivity of the GM when it is viewed in these terms.

8.2.3 Thermal reactivity of the GM dimer
Concentrated GM samples are resistant to thermally induced hydrolysis: the thermal energy is consumed in breaking down the dimeric association. The concentration of monomers will increase with temperature but not to the same degree as the dilute sample. The formation of monomers results in a small percentage of the sample being hydrolysed. The reactivity of the hydrolysates appears to be directed by the concentrated nature of the solution and the condensation products are of a higher order than the disiloxane species found in the dilute sample.

8.2.4 Thermal Reactivity of the GM Monomer
The dilute GM sample hydrolyses more readily than concentrated samples. This is expected as the monomer will hydrolyse more readily and the dilute solution contains a higher percentage of monomers. However when the sample is brought to the application temperature, the condensation products are limited to the formation of the preliminary T₃ siloxanes.

8.3 The Interaction between the GM and the Substrate

8.3.1 The interaction of the GM and the Mild Steel Substrate
XPS results indicate that the GM condensate deposits at the MPMSL. However the amount of the GM deposited is not enough to completely cover the substrate surface. Also, on visual inspection there is no visible difference to the surface before or after the
heat treatment with the GM. This fact is further emphasised by the inability of the Anasys Team to record a satisfactory spectrum from the heat treated GM-MPMSS surface.

8.3.2 Complex Substrates: Zinc Phosphate Conversion Coating on Mild Steel

The analysis of the Henkel 958+ ZPCC has revealed that the coating dehydrates during thermal stress. There is oxidation of either the Fe substrate or metallic inclusions from the phosphating bath caused by thermal stress. It is expected that the GM will be hydrolysed more fully by a substrate that contains water as a result of its preparation and releases this water as it is heated. The interaction of the GM nitroso group with Zn ions in the tricationic coating must also be taken into account. Nitroso containing compounds will form coordination complexes with Zn and such an interaction between the GM and the ZPCC cannot be overlooked.

8.4 The GM Nitroso Reactivity

8.4.1 Solution NMR Results for the GM Nitroso Reaction with Ene Substrates

The principle finding from the investigation of the reactivity of the GM nitroso moiety and ene substrates is that the nitroso functional group will convert to a nitro group in conditions where it is heated in the presence of both an ene substrate and oxygen. As is seen from the reactions carried out in this body of work, the presence of oxygen results in the conversion of the nitroso group to a nitro group in the presence of the ene substrate. In chapter 3, no such conversion was detected in samples where the GM was heated to the application temperature; the nitroso functional group remained unchanged after heating. In the context of the project, this rules out the inclusion of ene substrates in the formulation if it is to be prebaked in ambient atmosphere prior to the injection moulding of the NR.
8.4.2 Infrared Spectroscopy: The GM in the Application Environment

The results from the injection moulded samples indicate a complex interaction occurs between the GM and the NR in the application environment. There are two key aspects to the GM-NR interaction.

Firstly, it has been shown that the GM mixes with the NR during the injection moulding process. The GM modified NR that results may or may not be covalently bonded together however it has been shown that the nitroso moiety has reacted to some extent during the mixing process with the GM. This GM modified NR appears to be absorbed into the body of the NR, IR spectroscopy of the vulcanizate surface indicating that the majority of the surface area was comprised of cured rubber in which no GM IR signal was detected.

Secondly, the NR modified by the GM releases vulcanizing sulphur additives during the injection moulding/curing process. Sulphate deposits were only detected in the vicinity of GM modified NR deposits on the MPMSS surface indicating that this was not a general reaction occurring between the NR and the MPMSS surface. The structure of the sulphate detected at the surface was temperature dependent: higher temperature curing favouring the formation of amorphous sulphates, lower temperature curing producing crystalline deposits.
Figure 8.3: The proposed mechanism for the behaviour of the GM-NR-MPMSS system in the injection moulding and curing environment.

(A) The GM Layer and the NR are in contact at the outset of injection moulding: the GM layer is immediately drawn into the body of the NR

(B) The GM mixes and reacts with the NR. Simultaneously, the elemental sulphur in the NR is deposited on to the MPMSS surface.

(C) The sulphate layer is formed at the site where the GM modified NR is in contact with the MPMSS.

The high pressure conditions at which the NR is introduced to the substrate would suffice to cause the absorption of the GM into the body of the NR. The subsequent reaction of the GM and the NR is then responsible for the release of sulphur based compounds form the NR which in turn forms sulphate deposits at the MPMSS surface.
8.5 The Effect of Thermal Stress on the Rubber to Metal Adhesive Formulation

The adhesion testing of the GM containing formulation at three different sample preparation temperatures has revealed the following.

The bond between the formulation and the NR vulcanizate showed an interfacial area where the carbon signal of the NR and the chlorine signal of the formulation overlapped. Silicon was not detected in this region and sulphur was seen to be lower in concentration in the vicinity of the interface. This may provide some interesting new insight to the Henkel team as to the manner in which the NR and formulation interact during bonding.

The samples that were injection moulded and cured at 160 °C exhibited weaker bonding to the mild steel substrate than those prepared at 140 °C and 120 °C. The samples prepared at 140 °C and 120 °C had similar bond strengths. SEM/EDX analysis has indicated that there is a thicker oxide layer under the formulation in the samples prepared at 160 °C. In some places this oxide has grown rapidly and breached the formulation surface, typically in areas where the rubber was removed fully from the formulation during the tensile strength testing.

8.6 Future Work

(a) Determine whether or not the dissociation constant of the GM hydrogen bonding can be quantified.

If so, solution studies would be recommended to determine the dissociation constant and also the effect that solution properties such as polarity have on this value.
(b) Examine the deposition of GM coatings on inorganic substrates from DMSO solutions.

From this work it may be seen that the concentration of silanol and siloxane species present in a GM DMSO solution can be controlled by adjusting the concentration of the solution and applying a subsequent thermal treatment. It is proposed that solutions of varying silanol/siloxane concentration are prepared and the coatings that are prepared from these solutions are characterised and compared. It is possible to remove the alcohol from the GM/DMSO solutions. This could be carried out to see what effect the solvent removal has on the stability of the GM/DMSO solutions.

(c) Synthesis and characterisation of urethane functionalised analogues of common alkoxy silane precursors such as MAPTMS, GPTMS & APTES.

The GM exhibits excellent stability in challenging chemical environments. This stability is a result of hydrogen bonding between the urethane secondary amine and carbonyl sites on the molecule. It is proposed that this interaction sterically hinders the formation of the pentacoordinate intermediate that plays a role in the hydrolysis reactions of alkoxy silanes. The stability provided by urethane hydrogen bonding is one that may be capitalised upon in the wider context of alkoxy silane coupling agents in industry as surface modifying treatments. It is common in industry to apply washes containing organofunctional alkoxy silanes to inorganic surfaces as a processing step. As outlined in the chapter 1, hydrolysis and condensation of organofunctional alkoxy silanes is a challenging and complex chemical process that sees many different reactions proceeding at a variety of rates and in parallel. These processes are also very sensitive to reaction conditions such as the choice of catalyst
and the ratio of aqueous and non-aqueous solvent in the reaction mixture. It is proposed that the stability provided by the incorporation of the urethane moiety can be introduced into this type of surface processing and provide improved compounds for the modification of surfaces in industrial processes.

For instance, by reacting 2-hydroxyethyl methacrylate with (3-isocyanatopropyl) triethoxysilane, a new surface modifying reagent is prepared that incorporates the urethane group and takes advantage of its impact on the reactivity of the alkoxysilane (Error! Reference source not found.). The same applies to any other organofunctionality commonly used in alkoxysilane surface treatments.

(d) Study the feasibility of a novel coating process using the stable urethane based silanol coating solutions.

During the course of this work it became apparent that a novel method for coating metallic substrates could be developed. Induction heating may be used to prepare a coating on a metal substrate immersed in a solution containing an alkoxysilane, silanol or siloxane compound. A schematic of the process is shown in Figure 8.4.
Figure 8.4: Coating apparatus that takes advantage of controlled induction heating of a metal substrate in a coating solution containing alkoxy silane, silanol or siloxane precursors.

Current is passed through the coil and induces heating in the metal part. The coating solution reacts with the substrate surface as the temperature of the substrate increases. The process has a number of parameters that can be changed in order to control the final composition of the coating including:

- Alkoxy silane/silanol/siloxane content of the coating solution
- Solvent applied in the coating solution
- Heating rates and maximum temperature of coating process
- Agitation of the coating solution, what impact will stirring have on the coating composition/morphology?

(e) Investigate the process of sulphur release from NR during the injection moulding process.

The release of elemental sulphur by the NR in the presence of the formulation during injection moulding is another avenue of investigation. If it is confirmed that this process is occurring when the NR and the adhesive formulation interact, there
may be scope to adjust the formulation to use the sulphur to improve the bond. It may also improve the adhesive bond if the sulphur is prevented from interacting with the mild steel surface.
Index of Abbreviations

IM1C
1-methyl-1-cyclohexene, 157
ACA
Alkoxysilane Coupling Agent, 27
AFMIR
Atomic Force Microscopy Infrared Spectroscopy, 58
APTES
(3-Aminopropyl)triethoxysilane, 224
ATR
Attenuated Total Reflectance, 57
C14PI
cis-1,4-polyisoprene, 43
DENa
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