

Mechanism for cross-linking polychloroprene with ethylene thiourea and zinc oxide

BERRY, Keith, LIU, Max, CHAKRABORTY, Khirud, PULLAN, Nikki, WEST, Andrew, SAMMON, Chris <<http://orcid.org/0000-0003-1714-1726>> and TOPHAM, Paul D.

Available from Sheffield Hallam University Research Archive (SHURA) at:

<https://shura.shu.ac.uk/9683/>

This document is the Accepted Version [AM]

Citation:

BERRY, Keith, LIU, Max, CHAKRABORTY, Khirud, PULLAN, Nikki, WEST, Andrew, SAMMON, Chris and TOPHAM, Paul D. (2015). Mechanism for cross-linking polychloroprene with ethylene thiourea and zinc oxide. *Rubber Chemistry and Technology*, 88 (1), 80-97. [Article]

Copyright and re-use policy

See <http://shura.shu.ac.uk/information.html>

A NEW MECHANISM FOR CROSS-LINKING POLYCHLOROPRENE WITH ETHYLENE THIOUREA AND ZINC OXIDE

KEITH BERRY,^{1,2} MAX LIU,² KHIRUD CHAKRABORTY,² NIKKI PULLAN,¹ ANDREW WEST,³

CHRIS SAMMON,⁴ PAUL D. TOPHAM^{1*}

1. CHEMICAL ENGINEERING AND APPLIED CHEMISTRY, ASTON UNIVERSITY, BIRMINGHAM, B4 7ET, U.K.

2. ROBINSON BROTHERS LTD., PHOENIX STREET, WEST BROMWICH, B70 0AH, U.K.

3. U.K. MATERIALS TECHNOLOGY RESEARCH INSTITUTE (A PERA TECHNOLOGY COMPANY), NOTTINGHAM ROAD,
MELTON MOWBRAY, LEICESTERSHIRE, LE13 0PB U.K.

4. MATERIALS AND ENGINEERING RESEARCH INSTITUTE, SHEFFIELD HALLAM UNIVERSITY, HOWARD STREET,
SHEFFIELD, S1 1WB, U.K.

ABSTRACT

An investigation into the mechanism by which ethylene thiourea (ETU) cross-links polychloroprene in combination with zinc oxide (ZnO) was undertaken. This was achieved through an examination of the mechanisms of cross-linking polychloroprene rubber (CR) with ETU and ZnO separately and in unison. Spectroscopic and physical characterisation techniques were employed to probe the cross-linking mechanisms of CR using other standard rubber accelerators and model compounds with analogous structures and functionalities to ETU. These investigations have resulted in the proposal of a new mechanism by which ETU and ZnO can synergistically cross-link polychloroprene, in addition to providing new evidence to support concomitant mechanisms already published for cross-linking polychloroprene.

INTRODUCTION

Polychloroprene was one of the first synthetic elastomers to be developed and it remains a vital material today.¹ The global capacity for polychloroprene in 1985 was over half a million tonnes,² a level that has remained fairly constant ever since.³ Polychloroprene has applications as wide-ranging as the automotive industry,⁴ construction industry,⁴ as adhesives⁴ and even as liner pads on missile launchers.⁵ To provide a final material with appropriate structural integrity and intrinsic strength, polychloroprene must be cured, or cross-linked. Polychloroprene cross-links differently to other diene rubbers due to the electronegative chlorine atom which inhibits the electrophilic substitution reaction that is common to the cross-linking mechanism of other unsaturated polymers. Therefore, due to these differences in cross-

linking mechanisms, the accelerators used to cross-link polychloroprene are also different. Common rubber accelerators [such as tetramethyl thiuramdisulfide (TMTD), *N*-cyclohexyl-benzothiazole-sulfenamide (CBS) and mercaptobenzyl thiazole (MBT)] are not able to cross-link polychloroprene, and ethylene thiourea (ETU) in conjunction with zinc oxide (ZnO) is the most commonly used accelerator system. A typical cure system to produce cross-linked polychloroprene rubber contains polychloroprene gumstock, zinc oxide/magnesium oxide, a curing accelerator (typically ETU), stearic acid (as a processing aid) and additives to control properties such as photo-degradation, thermal stability and colour. Whilst such cure systems have been widely used for many years, the precise roles of the ZnO and the mode of action of the accelerator remain uncertain. It is believed that the metal oxides act as acid scavengers and help to protect the cured rubber against degradation by hydrochloric acid, which can be produced during cross-linking.⁶ However, it has been shown that ZnO is capable of promoting the formation of cross-links within the gumstock and therefore acts as a curing accelerator in its own right.⁷⁻⁸ A number of mechanisms have also been proposed for the mode of action of ETU, with supporting analytical evidence supplied in each case.⁹

The precise manner in which ETU accelerates the cross-linking of polychloroprene is of interest scientifically and because of the toxic nature of the compound. ETU is classified as a carcinogenic and potentially mutagenic and reproductive toxin¹⁰ and has recently been added to the candidate list for classification as a substance of very high concern by the European Community (EC).¹¹ As such, the use of ETU is subject to review and potential phasing out within member states of the European Union. However, in order to replace ETU with a safer alternative with similar abilities in curing polychloroprene, one must understand how it functions as an accelerator. Detailed knowledge of this will allow the design of replacement molecules that have similar cure efficiencies to ETU, but will crucially not have associated toxicity issues.

Polychloroprene (CR) was one of the first synthetic elastomers to be developed¹² and cross-links in a different manner to most other elastomers. There are four isomers present within CR (shown in Figure 1),¹³⁻¹⁶ but it is the 1,2-isomer which is central to the cross-linking process,^{7, 17-22} due to its propensity to undergo allylic rearrangement.²³ There have been several cross-linking mechanisms for polychloroprene published in the literature; the two most prevalent are the bis-alkylation mechanism using ETU alone proposed by Kovacic²⁴ and the synergistic mechanism with ETU and ZnO initially suggested by Pariser.²⁵ The bis-alkylation mechanism involves ETU reacting directly to form a cross-link through the two nitrogen atoms, evolving hydrochloric acid (HCl) as a by-product. According to the Pariser mechanism, where both additives are adopted, ETU reacts with the polymer chain through its sulfur atom and then ZnO reacts with the 'pendant ETU' to yield ethylene urea (EU) and zinc chloride (ZnCl₂) by-products. Consequently, a sulfur cross-link bridge forms between the polymer chains. Additional published mechanisms for cross-linking CR are concerned with

cross-linking CR with ZnO only, such as the cationic mechanisms proposed by Desai *et al.*¹³ and Vukov,²⁶ the 'ether-linkage' formation theory⁹ and the mechanism proposed by Mallon *et al.*,¹⁴ whereby the 1,2-isomer, which had not undergone allylic rearrangement, was able to take part in the cross-linking process.

Herein, we report a thorough study of the cross-linking of polychloroprene using FTIR spectroscopy and physical property characterisation to investigate a range of pre- and post-cured blends, in addition to *in situ* studies during the curing process. We present our evidence for polymer backbone isomerisation by ZnO and ETU and the formation of both carbon-carbon and carbon-sulfur cross-links. Finally, we propose a new mechanism for the mode of action of ETU, which is supported by our experimental evidence.

EXPERIMENTAL

The polychloroprene gumstock was Denka S40V (CR, Denka, Japan). Oligochloroprene with a molecular weight of 3000 g/mol was synthesised by free radical polymerisation at 55 °C for 17 hours using 1-dodecanethiol as a chain transfer agent (Sigma-Aldrich, UK) and α,α' -azoisobutyronitrile as the initiator (AIBN, Molekula, UK), in toluene (25 % v/v with respect to chloroprene). Additional chemicals used in this project included ethylene thiourea (ETU, Linkwell, UK), zinc oxide (ZnO, pharma grade, Durham Zinc Chemicals, UK), tetramethyl thiuramdisulfide (TMTD, Omya, UK), mercaptobenzyl thiazole (MBT, Omya, UK), stearic acid (Croda, UK), 1,8-octanedithiol (ODT, Sigma-Aldrich, UK), 1,4-diaminobutane (DAB, Sigma-Aldrich, UK), dibutyl thiourea (DBTU, Sigma-Aldrich, UK), ethylene urea (EU, Sigma-Aldrich, UK), methanol (MeOH, Sigma-Aldrich, UK) and hydrochloric acid (HCl, Sigma-Aldrich, UK). Static Fourier-Transform infra-red (FTIR) spectra were obtained in the solid state using a Thermo Scientific Nicolet iS10, employing ATR on a diamond crystal plate for 32 scans with a resolution of 4.0 cm⁻¹. Dynamic FTIR spectra, obtained whilst curing, were obtained on a Thermo Nicolet Nexus, set automatically to collect spectra every 30 seconds using a Golden Gate ATR accessory. Spectra were collected as a single beam of 16 scans with a resolution of 4.0 cm⁻¹, in the range 600-4000 cm⁻¹, and then normalised against the background or the initial uncured sample. Rheology was performed on a Monsanto MDR 2000E with an oscillating frequency of 1.667 Hz. Tensile samples were tested on an Instron 4302 and pulled according to BS903: Part 2A: Type 1 Dumbbells (Large). All compounding was complete within 15 minutes, adopting a two-roll mill with a friction ratio of 1:1.25 and utilising cooling water. Potential impurities and cross-linking by-products were removed by methanol soxhlet extraction, which proceeded for 8 hours, unless stated otherwise. As is standard in the rubber industry, additives were measured by weight with respect to the

polymer used, with units of parts per hundred of rubber (phr). All tests were carried out in pure polychloroprene gumstock with 0.6 phr stearic acid and no other additives except those quoted in the text.

RESULTS AND DISCUSSION

Examination of the rheological properties of polychloroprene rubber (CR) cured with ETU and ZnO show that a synergistic cross-linking process is in effect when these additives are used in conjunction with each other (Table I). This is shown by increases in the maximum torque and the cure rate. Therefore, to fully understand the mechanisms that occur during cross-linking, both ETU and ZnO have been examined as cross-linking agents individually, and in unison.

CROSS-LINKING POLYCHLOROPRENE WITH ZINC OXIDE

When ZnO alone is used to cure polychloroprene (Table I), the rubber is seen to cross-link at 160 °C through the cure rate and maximum torque recorded after 15 minutes at this temperature. FTIR analysis of the purified rubber (*via* methanol soxhlet extraction) reveals a peak at $\sim 1580\text{ cm}^{-1}$ (Figure 2), which is not present in the spectrum of uncured polychloroprene rubber. A peak in this region is on the border for a diene C=C stretch,²⁷⁻²⁹ particularly when attached to an electron withdrawing group, however, a π cloud interaction due to the formation of a co-ordination complex with zinc would reduce the wavenumber for a C=C³⁰⁻³² allowing the peak to appear in this region thus showing that a carbon-carbon double bond is formed upon vulcanisation, either as part of the actual cross-link, or elsewhere in the polychloroprene chain, after the 1,2-isomer rearrangement. *In situ* FTIR data, depicted in Figure 3, shows a change in height of the 1580 cm^{-1} peak during the curing process. A maximum is achieved within approximately four minutes, followed by a steady reduction in peak height until a plateau is reached after approximately 20 minutes (at *ca.* half of the maximum intensity, yet significantly higher than the starting intensity). This suggests that unsaturation occurs as an initial step in the cross-linking process, but that the level of unsaturation decreases upon further cross-linking, such that half of the unsaturated moieties have reacted by the end of the curing process.

Several groups^{7, 33} have disproved the ether-linkage formation mechanism, which is described by Hofmann.¹⁷ If this mechanism were to proceed, a strong band in the $1085\text{-}1150\text{ cm}^{-1}$ region of the FTIR spectrum would be expected.^{27, 34} No such peak has been detected herein (see Figure 2), which provides further evidence against this theory.

Through observing the change in peak height of the $\sim 925\text{ cm}^{-1}$ band over time (associated with stretching of C-C adjacent to the C=C in the 1,2-isomer, shown in Figure 4), it can be seen that the 1,2-isomer of CR is able to rearrange

upon heating at 160 °C for approximately 40 minutes without the addition of any curing additives. However, rearrangement occurs much faster when ZnO is present. Figure 4 shows that with ZnO, the 1,2-isomer undergoes approximately 90 % allylic rearrangement within a minute and total rearrangement is complete after just two minutes. Crucially, these results disprove the theory of Mallon *et al.*,¹⁴ who states that the 1,2-isomer (pre-rearrangement) takes part in the cross-linking reaction, and that cross-linking ceases once all of the 1,2-units have been rearranged. In contrast, the scorch time (Table I, TS1) of over two minutes obtained herein for CR with ZnO indicates that cross-linking has not commenced within this time, while the results in Figure 4 show that all of the 1,2-isomer has already rearranged within 2 minutes. This proves that cross-linking can only occur with the rearranged 1,2-isomer, owing to the fact that all of the 1,2-isomer has rearranged before the onset of cross-linking.

Appearance of the 1580 cm⁻¹ peak in the FTIR spectrum on cross-linking CR (Figure 2) supports the theory of Vukov.²⁶ This cationic mechanism, which was based on model compounds and work with halo-butyl rubber, suggested that diene formation was the major reaction after rearrangement of the 1,2-isomer, where the diene aided cross-linking. Intensity reduction of this key 1580 cm⁻¹ peak, after it reaches a maximum, indicates that the diene formed during the process is undergoing further reaction; adding further evidence for the Vukov mechanism. Scheme 1 shows this mechanism with polychloroprene, (the original mechanism was detailed with model compounds).

CROSS-LINKING POLYCHLOROPRENE WITH ETHYLENE THIOUREA

CR was cured with several different model compounds, including (i) traditional rubber accelerators, such as tetramethyl thiuramdisulfide (TMTD), (ii) amine-containing species, such as 1,4-diaminobutane (DAB), and (iii) sulfur-containing compounds, such as 1,8-octanedithiol (ODT). Figure 5 shows the structures of the different model compounds adopted. Rheological data (Table II) show that traditional rubber accelerators, TMTD and mercaptobenzyl thiazole (MBT) when used with no other additives, such as ZnO, are unable to cross-link CR, even though TMTD contains an N-C=S functionality analogous to that of ETU. However, it is known that TMTD requires activation when cross-linking natural rubber (NR), whereas ETU does not require activation to cross-link polychloroprene. Ethylene urea (EU) is also unable to cross-link CR, despite having a similar structure to ETU (simply with oxygen in place of the sulfur atom); this can be attributed to the difference in electronegativity of oxygen compared to sulfur. Oxygen withdraws electron density more strongly, rendering the nitrogen atoms less nucleophilic (i.e. it is more difficult for the lone pair on the nitrogen to attack an electrophilic site). This effectively prevents the nitrogen atoms reacting and participating in the cross-linking reaction. Dibutyl thiourea (DBTU), which is also very similar structurally to ETU, with the bridging ethylene group in ETU replaced by two butyl groups, is able to cross-link CR, but not to the same extent as ETU. This is due to the two

amino moieties on DBTU being more sterically hindered, rendering them less likely to undergo cross-linking reactions. To ascertain the 'linking' site on the accelerator (*i.e.* nitrogen or sulfur), two linear alkyl chains with chain end primary functionality were tested; 1,4-diaminobutane (DAB) and 1,8-octanedithiol (ODT). DAB has amino groups at each chain end and was capable of cross-linking, whilst ODT, with thiol groups at each end was not. In short, our findings indicate that it is the nitrogen atoms within the ETU molecule that are taking part in the cross-linking reaction, due to the failure of the sulfur-containing model compounds.

In addition to studying mechanical properties, the use of FTIR spectroscopy to compare cured and uncured polychloroprene samples containing ETU was undertaken. One of the most notable bands that appears in the FTIR spectrum after cross-linking polychloroprene with ETU is that formed at $\sim 1550\text{ cm}^{-1}$ (Figure 6). After soxhlet extraction of the cross-linked rubber with methanol this band was still present, confirming that it was not caused by an extractable impurity or by-product. This new peak is different to that found when ZnO cross-links polychloroprene alone, which is seen at 1580 cm^{-1} , and is consistent with a newly formed C=C bond. The structure of polychloroprene when reacted with ETU is clearly different to that when ZnO alone acts as a cross-linker. When polychloroprene is cured with ETU, the height of the 1550 cm^{-1} peak in the FTIR spectrum, when monitored over time, increases rapidly over the course of the first two minutes cure time, followed by a slower increase over the remaining *ca.* 28 minutes of cure (Figure 7). These results indicate a high degree of initial cross-linking activity and that the rate of cross-linking decreases as ETU is consumed. Also, it should be noted that the increase in cross-linking activity, as demonstrated by FTIR analysis, follows a similar trend to the rheograph of ETU cross-linking polychloroprene (Figure 7). These results suggest that the 1550 cm^{-1} peak is intimately linked with the cross-linking activity of ETU and is associated with a final cross-linked product; most likely a $\nu(\text{C}=\text{C})$ that is weakened by the electron withdrawing capacity of the adjacent ETU moiety, resulting in a *ca.* 30 cm^{-1} shift when compared to the $\nu(\text{C}=\text{C})$ species generated in the ZnO cross-linked system.^{29, 35-36}

One of the by-products from the cross-linking mechanism proposed by Kovacic is HCl.²³ It is difficult to monitor the formation of such by-products when cross-linking in CR, but simpler to do so with low molecular weight oligomer. This is firstly because polychloroprene rubber has a relatively high molecular weight ($M_n \sim 250,000\text{ g/mol}$) and reactions occurring in the polymer are thus difficult to monitor as cross-linking renders the material insoluble. In contrast, oligomers can be readily dissolved because they instead become heavily branched, rather than cross-linked. Examination of the cross-linking of polychloroprene rubber *in situ* is also difficult because it is cured in an enclosed heated press, to ensure uniform curing throughout the sample. Oligomers can, however, be reacted simply in a test tube, which is more practical. For example, the pH of the headspace above the reaction mixture in the test tube can be monitored, whereas this test is more difficult to undertake in a sealed, pressurised vessel. Accordingly, the cross-linking

of oligochloroprene ($M_n \sim 3000$ g/mol) with ETU yielded an acidic environment almost immediately, which is attributed to the release of HCl during cross-linking.

The evidence gathered up to this point largely substantiates the bis-alkylation mechanism of Kovacic²³ (shown in Scheme 2) including; (i) the acidic environment created when ETU is used to cross-link oligochloroprene, (ii) the new peak (at 1550 cm^{-1}) in the FTIR spectrum (associated with a $\nu(\text{C}=\text{C})$, shifted due to the ETU moiety), which does not disappear on soxhlet extraction, thus indicating the formation of this new bond during the curing process, and (iii) evidence that the cross-link bridge must be through the nitrogen atoms, as the sulfur-containing model compounds (ODT and TMTD) were unable to react with the polymer chain on their own.

CROSS-LINKING POLYCHLOROPRENE WITH ETHYLENE THIOUREA AND ZINC OXIDE

Rheological properties of CR cross-linked with 5 phr ZnO in combination with the previously trialled model compounds, show significant disparities to when ZnO is absent (Table III). However, both EU and MBT are still incapable of cross-linking CR (in the presence of ZnO) any more so than would be achieved by ZnO alone. DAB is able to cross-link CR, but does so to a similar extent to when it is used as a cross-linker on its own, indicating that the addition of ZnO does not improve its cross-linking ability. Adopting sulfur-containing compounds, namely DBTU, TMTD and ODT, offers the most interesting results, however. The cross-linking of CR with these compounds, in combination with ZnO, is vastly improved, with cure rates and highest torques greater than those of CR cured with any of these additives separately. This is most evident in the results for ODT and TMTD, both of which were unable to cross-link CR at all on their own, yet both are capable in the presence of ZnO. These results demonstrate the significance of the sulfur atom in cross-linking CR, when implemented in combination with ZnO. The vital role that ZnO plays in activating sulfur-containing compounds is also highlighted in these results. Rheological curves of polychloroprene cured with various additives have differences, with the ETU/ZnO joint system being the only system where the curve reaches a plateau; all of the other cure curves show a marching modulus. This indicates that ETU/ZnO provides the best curing system for polychloroprene.

When ETU and ZnO were used to cross-link polychloroprene separately, changes were observed in the 1500 to 1600 cm^{-1} region of the FTIR spectra between the cured and uncured CR samples. The system comprising ETU produced a peak around 1550 cm^{-1} , whereas the ZnO-containing formulation produced a peak around 1580 cm^{-1} . Unsurprisingly, when a combination is used to cross-link polychloroprene, both of these new peaks form and are both

still visible after the rubber has been subjected to soxhlet extraction with methanol (Figure 8). The appearance of the peaks at 1550 cm^{-1} and 1580 cm^{-1} indicates that the mechanisms by which each of these two additives (ETU and ZnO) cross-link polychloroprene alone are also taking place when they are used together, in addition to the occurrence of a third synergistic mechanism. It also confirms that the peaks do not have the same source. The 1498 cm^{-1} peak, seen in Figure 8, is associated with ETU, and its disappearance is due to the reaction of ETU during cross-linking and removal of any excess by soxhlet extraction.

The change in height of the 925 cm^{-1} peak in the FTIR spectrum over time, associated with the 1,2-isomer, has been plotted for the cross-linking reaction of CR with ETU and ZnO (Figure 9). It can be seen that the ZnO-only system and ETU/ZnO combined system promote the rearrangement of the 1,2-isomer much quicker than the ETU only system. A comparison between the ETU/ZnO system and the ZnO-only system shows that rearrangement of 90 % of the 1,2-isomer proceeds at a similar rate, however the final 10 % of the isomer takes approximately 8 minutes longer when ETU is present. However, both of these results indicate that ZnO interacts with the polymer chain faster than, and thus before, ETU. In doing so, ZnO rearranges the 1,2-isomer, which is the crucial first step in these polychloroprene cross-linking mechanisms.

To ascertain the by-products formed in the cross-linking reaction, a sample of polychloroprene cured with ZnO and ETU was purified using methanol soxhlet extraction and the extracts were examined by both gas chromatography-mass spectrometry (GC-MS) and thin layer chromatography (TLC). GC-MS revealed a mass ion of 86 g/mol at a retention time of 50.43 minutes, which correlates with the molecular mass of ethylene urea (EU). TLC was undertaken with ethyl acetate as the eluent and the results compared to a reference sample of EU, both affording retention factors of 0.05. FTIR analysis of the extract following removal of methanol *in vacuo* confirmed the presence of EU, although the extracts also contained ETU (Figure 10A). Confirmation came *via* the characteristic $\nu(\text{C}=\text{O}) \sim 1670\text{ cm}^{-1}$ associated with the carbonyl group in EU. The same peak at 1670 cm^{-1} in the FTIR spectrum is seen when a 1:1 (w/w) mixture of EU and ETU powder are mixed together and analysed (Figure 10B).

When oligochloroprene was heated at $160\text{ }^{\circ}\text{C}$ with ETU and ZnO to simulate cross-linking, a white solid was precipitated within 10 minutes. The peaks in the FTIR spectrum associated with the unreacted oligomer were subtracted using Omnic v6.2 software, which yielded a spectrum of the modified component of the oligochloroprene (Figure 11A). The solid formed was found to comprise an adduct of ETU and zinc chloride (ZnCl_2) (Figure 11B). This was ascertained when ETU, ZnO and HCl were mixed together in various combinations and heated to $160\text{ }^{\circ}\text{C}$; the resultant mixtures were washed with methanol and also examined by FTIR spectroscopy. The spectrum which correlated most with the solid formed in the oligomer came from a mixture of all three chemicals (ETU, ZnO and HCl). ZnCl_2 was also

found to form when ZnO and HCl were mixed (found in a separate experiment). Consequently, ZnCl₂ was mixed with ETU, heated and washed with methanol and the product furnished a similar FTIR spectrum to that of the solid formed in the oligomer. Therefore, for this adduct to be formed, ZnCl₂ must be formed, and thus provides further evidence for the formation of ZnCl₂ during oligomer cross-linking.

The mechanism of Pariser²⁵ (shown in Scheme 3) is the standalone theory currently existing for cross-linking polychloroprene with ETU and ZnO in conjunction with each other. This study has yielded results which do not fully correlate with Pariser. For instance, we have shown that ZnO rearranges the 1,2-isomer quicker than ETU, indicating that ZnO interacts with the polymer chain first. In contrast, the Pariser mechanism indicates that ETU interacts with the polychloroprene polymer chain first, with ZnO reacting at a later stage. The vital role of ZnO as an accelerator has been proven in the studies using model compounds, whereby thiols have been unable to react with the CR polymer chain on their own, but have been capable when combined with ZnO. Similarly, thiurams cannot react with the polymer chain on their own, but are able to do so in the presence of ZnO. Such sulfur-containing compounds thus need the chain to be activated first (by ZnO). Dibutyl thiourea (DBTU) also cross-links very poorly on its own, but very well in the presence of ZnO. This is due to the butyl groups, whereby steric hindrance prevents DBTU from cross-linking polychloroprene efficiently through its nitrogen atoms *via* the bis-alkylation mechanism, which ETU alone achieves. However, in the presence of ZnO, DBTU can cross-link polychloroprene efficiently, as the steric hindrance is much less prevalent for the sulfur atom than the nitrogen atoms. Again, ZnO needs to be present to activate the chain for DBTU to cross-link *via* its sulfur atom, which proves to be the case with ETU as well. These results suggest that when ZnO is present, as ETU is unable to react with the polymer chain *via* sulfur, ZnO must activate the polymer chain first, allowing ETU to interact with the activated chain *via* the sulfur atom. Therefore, this activation of the chain (by ZnO) must be the first step in the cross-linking reaction, creating a sulfur bridge between polymer chains. This contradicts the Pariser mechanism, which shows ETU reacting with the polymer chain (through sulfur) as the initial step in cross-linking polychloroprene. Furthermore, if ETU were to react with the polymer chain *via* the sulfur initially, as suggested by Pariser, the next step would be for the completion of the cross-link through one of the nitrogen atoms in ETU to another chain (irrespective of the presence of ZnO). However, evidence showing the formation of EU implies that this does not occur.

As a result of the extensive evidence gathered throughout this study, a new mechanism is proposed for the cross-linking of polychloroprene with ETU and ZnO, which is provided in Scheme 4. In this mechanism, the 1,2-isomer rearranges first (as is generally accepted), followed by ZnO creating an active site on the polymer chain through substitution of the chlorine atom with oxygen. This then enables cross-linking through the sulfur atom of ETU. After these initial stages,

the remainder of the mechanism follows the route of that proposed by Pariser. It has also been found that it is possible for thiuram-based accelerators to cross-link polychloroprene in this manner, once they have been activated by ZnO. It is proposed that three mechanisms are in effect during the cross-linking of polychloroprene by ETU and ZnO; the three different routes are shown in Figure 12.

CONCLUSIONS

The mechanisms by which ETU and ZnO cross-link polychloroprene, individually, and in combination with one other, have been investigated. Results herein suggest that ZnO alone cross-links polychloroprene *via* a cationic mechanism, most likely through that proposed by Vukov.²⁶ Evidence for this includes the appearance of the 1580 cm⁻¹ peak in the FTIR spectra on curing, which is typically ascribed to a carbon-carbon double bond. Evidence is also provided that mechanisms, such as the formation of an ether linkage and the mechanism proposed by Mallon *et al.*,¹⁴ do not occur.

When cross-linking occurs with ETU alone there is evidence supporting the bis-alkylation mechanism proposed by Kovacic.²³ This includes the acidic environment detected when ETU cross-links oligochloroprene, signifying the generation of HCl. Also, a new peak in the FTIR spectrum is formed at 1550 cm⁻¹ which remains present after soxhlet extraction, indicating that a new chemical bond is formed during curing. This can also be ascribed to a carbon-carbon double bond that has been somewhat shifted due to the proximity of the incorporated ETU moiety. Furthermore, there is indirect evidence that the cross-link bridge is formed through the nitrogen atoms as model sulfur-containing compounds and thiuram-based accelerators were unable to react with the polymer chain on their own.

Finally, the cross-linking reaction when both ETU and ZnO are present in polychloroprene was examined. It has been verified that the mechanism employed by each of the reagents separately is occurring (Kovacic and Vukov). Likewise, there is evidence that at least a third mechanism is in operation. This particular mechanism comprises the formation of EU and ZnCl₂, as seen in the mechanism proposed by Pariser.²⁵ However, the mechanism of Pariser indicates that the sulfur atom of ETU reacts with the polymer chain first. Our evidence disproves this. Compounds containing a thiol group are only able to react with the polymer chain in the presence of ZnO, once an active site has been created. Therefore, the results herein indicate that a third new mechanism is indeed in effect. This mechanism is similar to that of Pariser, but crucially ZnO reacts first with the polymer chain ahead of ETU.

ACKNOWLEDGEMENTS

The authors thank the EPSRC for supporting this work through a CASE studentship with Robinson Brothers Ltd., and Pera Technology Ltd. for project sponsorship.

REFERENCES

1. Brydson, J. A., *Rubber Chemistry*. Applied Science Publishers Ltd.: London, 1978.
2. Hofmann, W., *Rubber Technology Handbook*. Hanser Publishers: New York, 1989.
3. Obrecht, W.; Lambert, J.-P.; Happ, M.; Oppenheimer-Stix, C.; Dunn, J.; Krüger, R., Rubber, 4. Emulsion Rubbers. In *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA: 2000.
4. DuPont DuPont™ Neoprene Polychloroprene.
<http://www.dupontelastomers.com/products/neoprene/neoprene.asp> (accessed 31st May 2013).
5. Meier, J. F.; Minter, H. F.; Connors, H. J., *J. Appl. Polym. Sci.* **15** (3), 619, (1971).
6. Glenn, F. E., Chloroprene Polymers. In *Encyclopedia of Polymer Science and Technology*, 4th ed.; John Wiley and sons, Inc.: 2005.
7. Miyata, Y.; Atsumi, M., *Rubber Chem. Technol.* **62** (1), 1, (1989).
8. Kawasaki, N.; Hashimoto, T., *J. Polym. Sci. Pol. Chem.* **11** (3), 671, (1973).
9. Akiba, M.; Hashim, A. S., *Progress in Polymer Science* **22** (3), 475, (1997).
10. Sebelius, K. *12th Report on Carcinogens*; U.S. Department of Health and Human Services: 2011.
11. ECHA Registry of Current SVHC Intentions. http://www.echa.europa.eu/web/guest/registry-of-current-svhc-intentions?search_criteria=Ethylene%20thiourea.
12. Catton, N. L., *The Neoprenes*. E. I. Du Pont De Nemours & Co. (Inc.): Wilmington, Delaware, 1953.
13. Desai, H.; Hendrikse, K. G.; Woolard, C. D., *J. Appl. Polym. Sci.* **105** (2), 865, (2007).
14. Mallon, P. E.; McGill, W. J.; Shillington, D. P., *J. Appl. Polym. Sci.* **55** (5), 705, (1995).
15. Okada, T.; Ikushige, T., *J. Polym. Sci. Polym. Chem. Ed.* **14** (8), 2059, (1976).
16. Ferguson, R. C., *J. Polym. Sci. Pt. A: Gen. Pap.* **2** (11), 4735, (1964).
17. Hofmann, W., *Vulcanization and Vulcanizing Agents*. Maclaren and Sons: London, 1967.
18. Das, A.; Naskar, N.; Basu, D. K., *J. Appl. Polym. Sci.* **91** (3), 1913, (2004).
19. Das, A.; Naskar, N.; Datta, R. N.; Bose, P. P.; Debnath, S. C., *J. Appl. Polym. Sci.* **100** (5), 3981, (2006).
20. Kato, H.; Fujita, H., *Rubber Chem. Technol.* **48** (1), 19, (1975).
21. Hepburn, C.; Mahdi, M. S., *Kautsch. Gummi Kunstst.* **39** (7), 629, (1986).
22. Sae-oui, P.; Sirisinha, C.; Thepsuwan, U.; Hatthapanit, K., *Eur. Polym. J.* **43** (1), 185, (2007).
23. Kovacic, P., *Ind. Eng. Chem.* **47** (5), 1090, (1955).

24. Kovacic, P., *Rubber Chem. Technol.* **28** (4), 1021, (1955).
25. Pariser, R., *Kunststoffe* **50** (11), 623, (1960).
26. Vukov, R., *Rubber Chem. Technol.* **57** (2), 284, (1984).
27. Pretsch, E.; Bühlmann, P.; Affolter, C., *Structure Determination of Organic Compounds - Tables of Spectral Data*. 3rd ed.; Springer - Verlag: 2000.
28. Williams, D. H.; Fleming, I., *Spectroscopic Methods in Organic Chemistry*. 4th ed.; McGraw-Hill Book Company: London, 1989.
29. Bellamy, L. J., *The Infra-red Spectra of Complex Molecules*. 3rd ed.; Chapman and Hall: London, 1975.
30. Powell, D. B.; Sheppard, N., *J. Chem. Soc.*, 2519, (1960).
31. Powell, D. B.; Sheppard, N., *Spectrochim. Acta* **13** (1), 69, (1958).
32. Chatt, J.; Duncanson, L. A., *J. Chem. Soc.*, 2939, (1953).
33. Kuntz, I.; Zapp, R. L.; Pancirov, R. J., *Rubber Chem. Technol.* **57** (4), 813, (1984).
34. Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W., *Tables of Spectral Data for Structural Determination of Organic Compounds*. 2nd ed.; Springer Verlag: New York, 1989.
35. Lord, R. C.; Walker, R. W., *J. Am. Chem. Soc.* **76** (9), 2518, (1954).
36. Jonassen, H. B.; Kirsch, W. B., *J. Am. Chem. Soc.* **79** (6), 1279, (1957).

TABLE I

15 MINUTE MDR RESULTS AT 160 °C FOR POLYCHLOROPRENE GUM-STOCK CONTAINING 5 PHR OF
ADDITIVE

	Gum stock ¹	ETU	ZnO	ETU and ZnO
Maximum torque, Nm	0.23	0.54	0.58	1.52
Scorch (TS1), mm:ss	00:00	01:33	02:40	00:53
T90, mm:ss	12:59	09:09	08:39	04:38
Cure rate, Nm/min	0.018	0.14	0.17	0.54

¹Gum stock contains 0.6 phr stearic acid only and has been milled.

TABLE II

RHEOLOGICAL PROPERTIES OF CR CURED WITH DIFFERENT ADDITIVES PRESENT AT 3 PHR.

15 minute MDR test at 160 °C

Additive	15 minute MDR test at 160 °C			
	Maximum torque, Nm	Scorch (TS1), mm:ss	T90, mm:ss	Cure rate, Nm/min
Ethylene thiourea (ETU)	0.46	02:01	10:02	0.09
Mercaptobenzyl thiazole (MBT)	0.19	-	12:32	0.05
Tetramethyl thiuramdisulfide (TMTD)	0.25	13:09	13:54	0.02
Dibutyl thiourea (DBTU)	0.38	03:26	11:21	0.06
1,4-diamino butane (DAB)	1.54	01:27	11:33	0.22
Ethylene urea (EU)	0.18	-	12:54	0.02
1,8-octane dithiol (ODT)	0.20	-	12:07	0.02

TABLE III

RHEOLOGICAL PROPERTIES OF CR CURED WITH 5 PHR ZINC OXIDE AND VARIOUS ADDITIVES

PRESENT AT 3 PHR.

Additive	15 minute MDR test at 160 °C			
	Maximum torque, Nm	Scorch (TS1), mm:ss	T90, mm:ss	Cure rate, Nm/min
Zinc oxide (ZnO)	0.58	02:40	08:39	0.17
Ethylene thiourea (ETU)	1.66	00:56	05:41	0.61
Mercaptobenzyl thiazole (MBT)	0.36	02:26	10:23	0.08
Tetramethyl thiuramdisulfide (TMTD)	0.86	00:55	06:01	0.75
Dibutyl thiourea (DBTU)	1.47	00:46	03:16	1.39
1,4-diaminobutane (DAB)	1.44	01:23	10:56	0.21
Ethylene urea (EU)	0.36	04:53	11:44	0.04
1,8-octanedithiol (ODT)	1.22	02:37	13:08	0.12

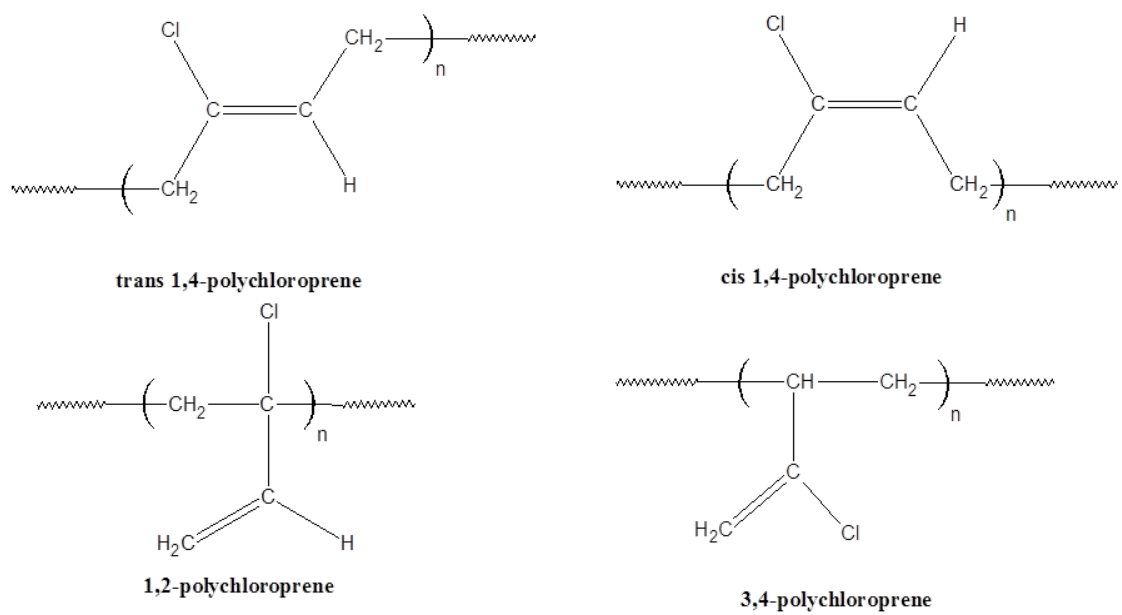


FIGURE 1. The four isomeric structures of polychloroprene.

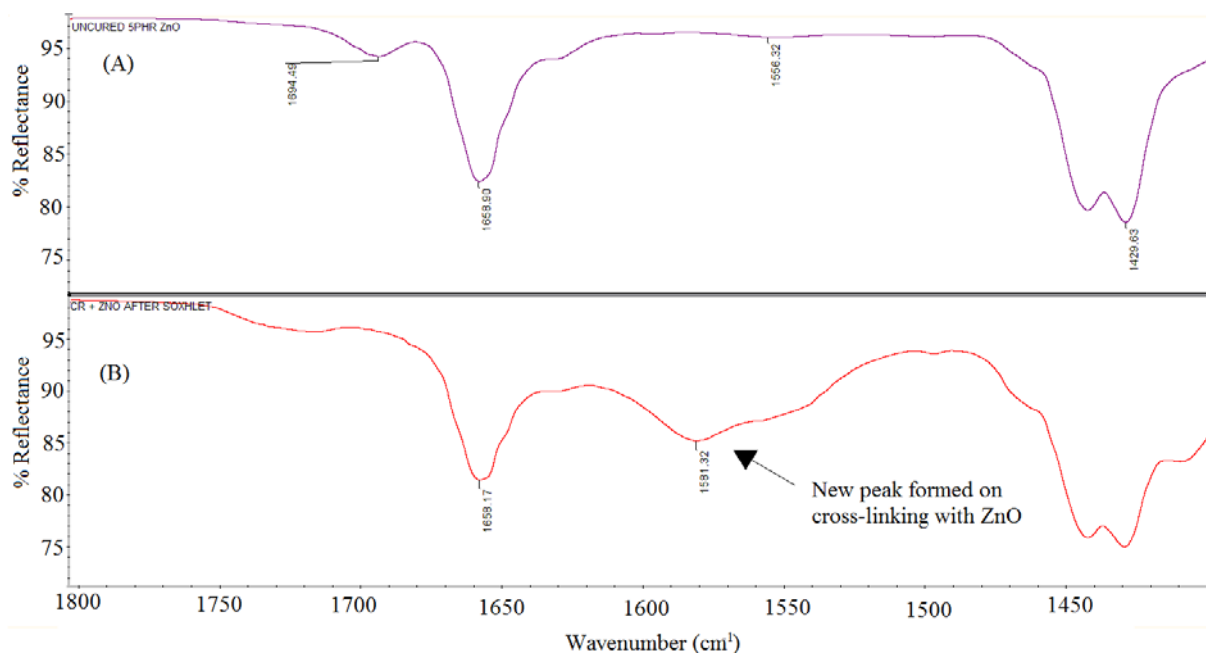


FIGURE 2. FTIR spectra of polychloroprene rubber with 5 phr ZnO, showing (A) uncured ZnO-containing polychloroprene rubber, and (B) after soxhlet extraction. Formation of a new peak at 1580 cm⁻¹ is clearly shown.

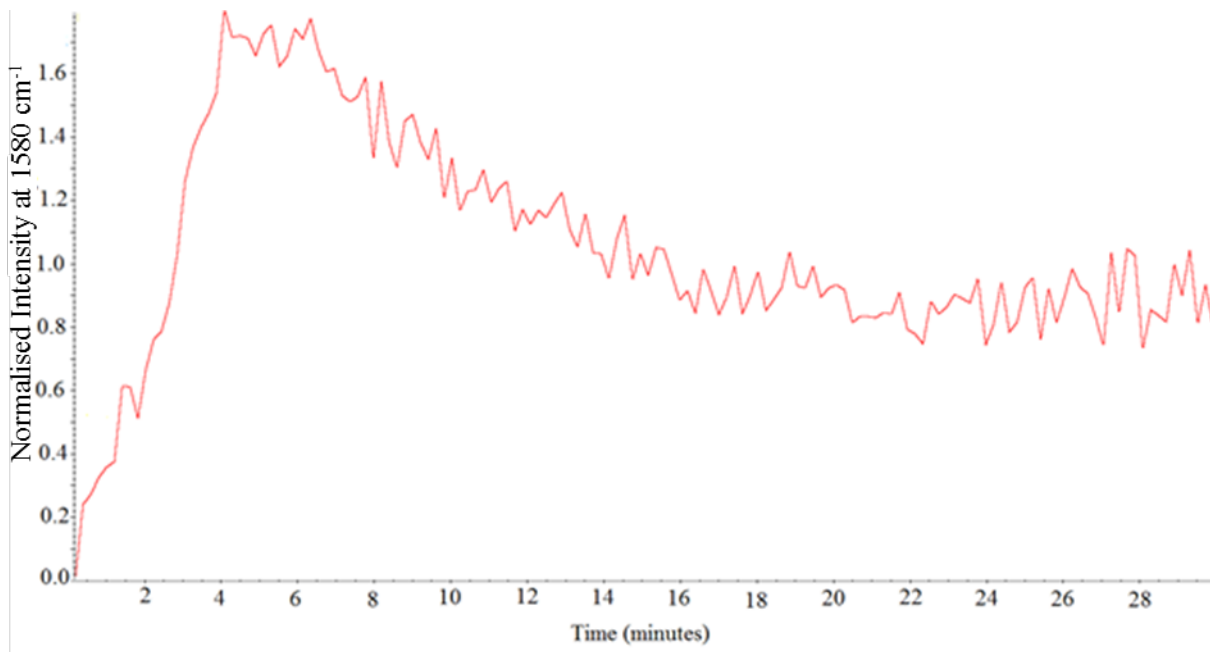


FIGURE 3. Change in height of the 1580 cm⁻¹ peak in polychloroprene with 5 phr ZnO as it cures at 160 °C.

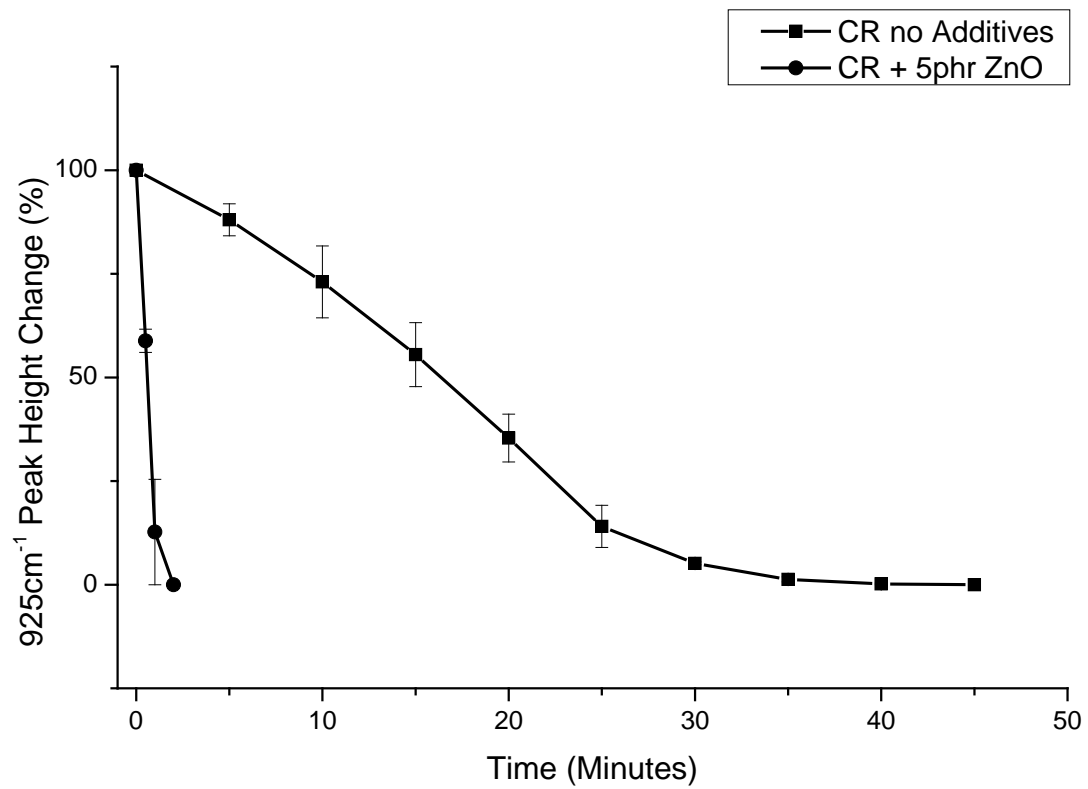


FIGURE 4. Change in height of 925 cm⁻¹ peak over time for polychloroprene containing ZnO. Note error bars show one standard deviation and are too minor to show above 30 minutes.

Compound	Structure
Tetramethyl thiuramdisulfide (TMTD)	
Mercaptobenzyl thiazole (MBT)	
Ethylene Urea (EU)	
Dibutyl thiourea (DBTU)	
1,4-diaminobutane (DAB)	
1,8-octanedithiol (ODT)	

FIGURE 5. Chemical structures of model compounds trialed.

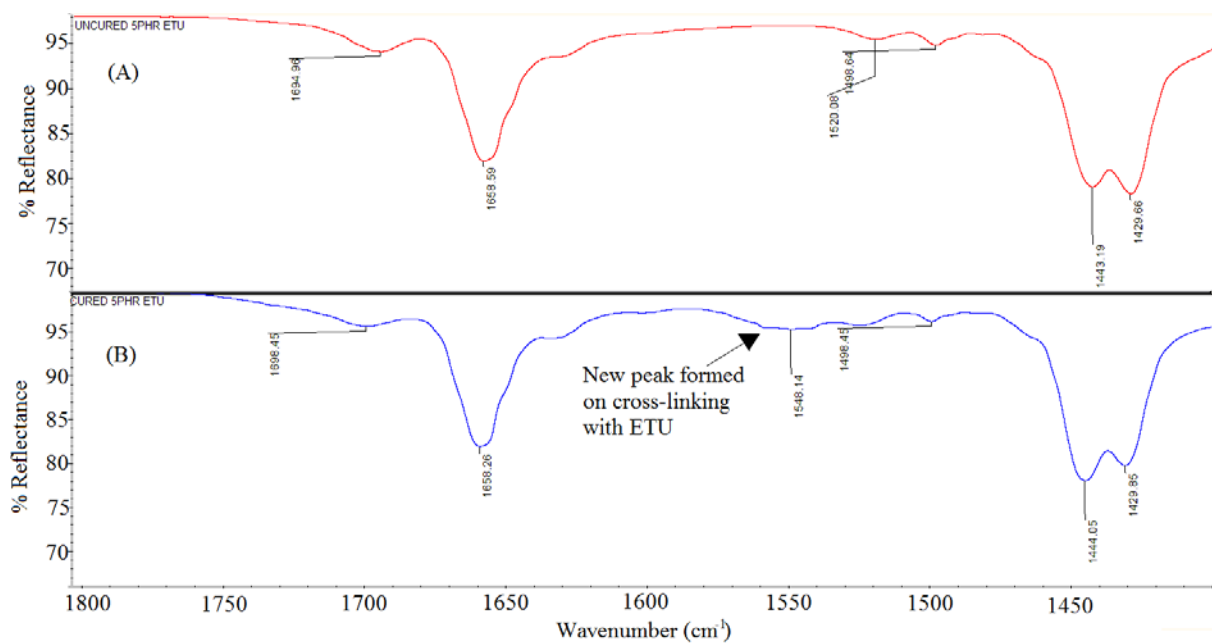


FIGURE 6. FTIR spectra of polychloroprene containing 5 phr ETU, (A) before curing and (B) after curing for the region 1400-1800 cm⁻¹. A new peak in the ETU cross-linked sample is shown at ~ 1550 cm⁻¹.

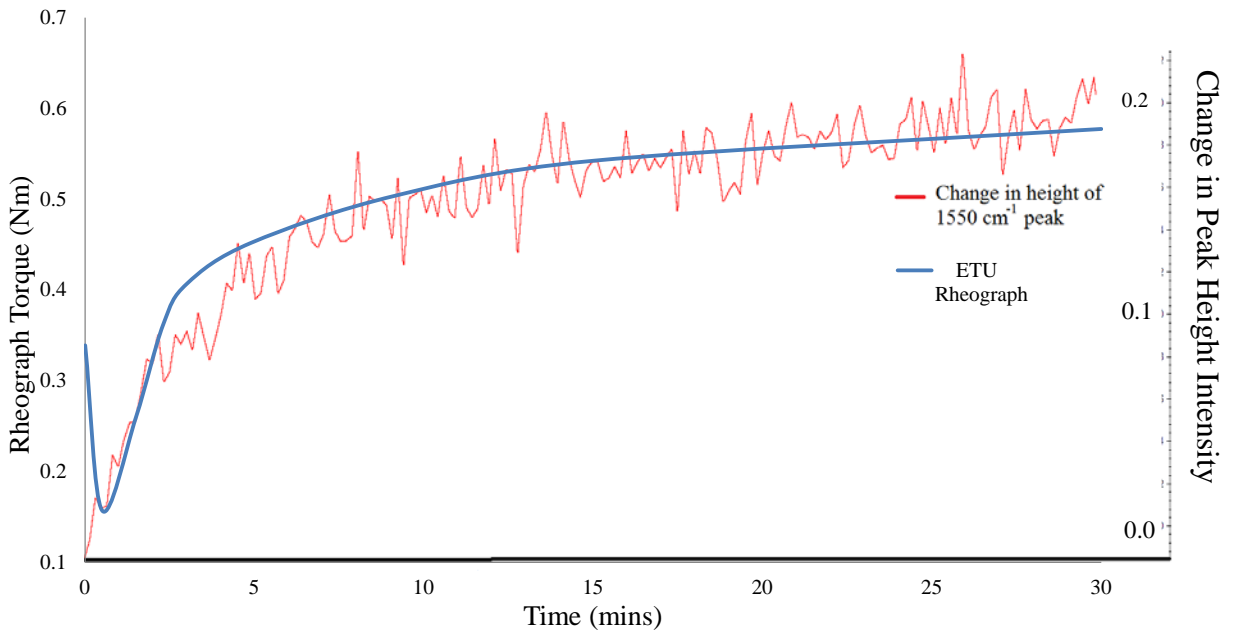


FIGURE 7. Change in the height of 1550 cm^{-1} peak in polychloroprene cured at $160\text{ }^{\circ}\text{C}$ for 30 minutes with 2 phr ETU compared to a rheograph of 2 phr ETU cross-linking polychloroprene at $160\text{ }^{\circ}\text{C}$.

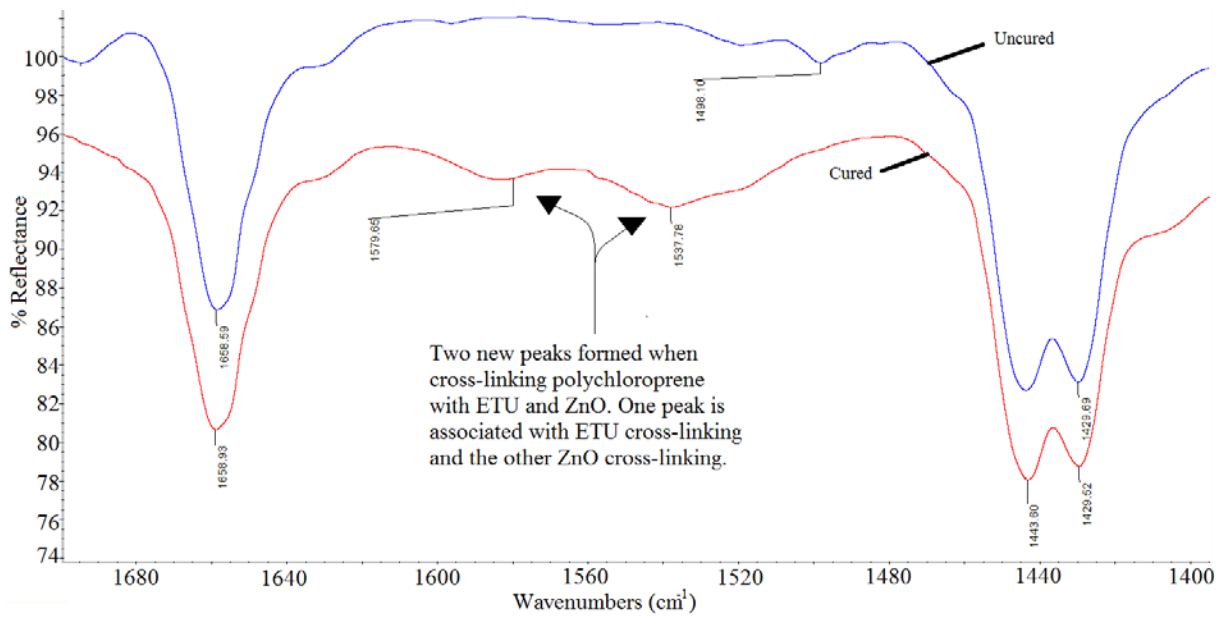


FIGURE 8. FTIR spectra showing new peaks at ~ 1540 and 1580 cm^{-1} when ETU and ZnO are used to cross-link polychloroprene. Spectra are shown from $1400\text{--}1700\text{ cm}^{-1}$ and are translated along the reflectance axis for clarity.

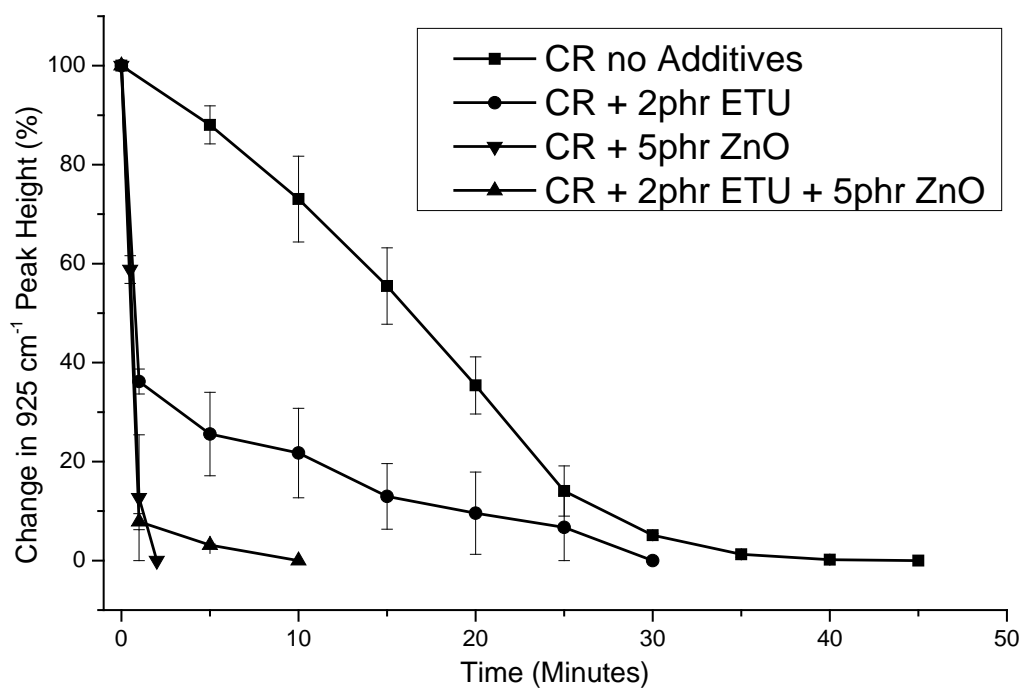


FIGURE 9. Change in height of the 925 cm^{-1} peak in polychloroprene as it cures at $160\text{ }^{\circ}\text{C}$ with ETU and ZnO as additives, compared to ETU or ZnO as separate additives and to pure polychloroprene. Error bars are one standard deviation and are not visible after 30 minutes.

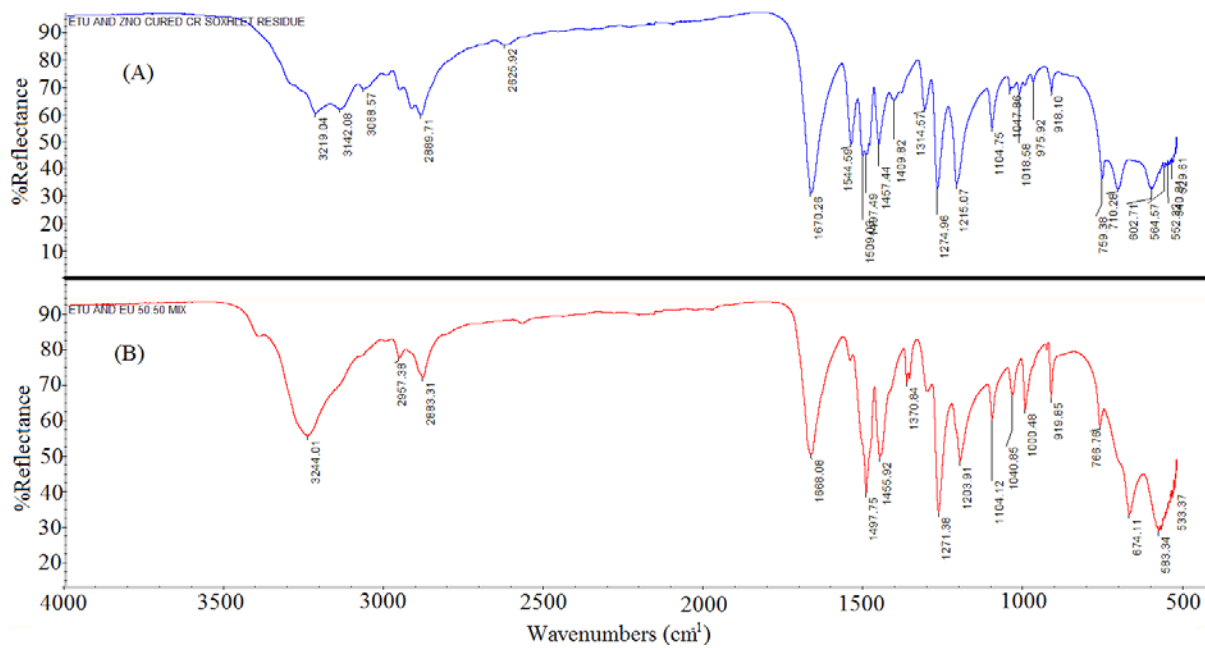


FIGURE 10. FTIR spectra showing (A) methanol soxhlet residue from polychloroprene cured with 2 phr ETU and 5 phr ZnO, and (B) a 1:1 (w/w) mixture of ETU and EU.

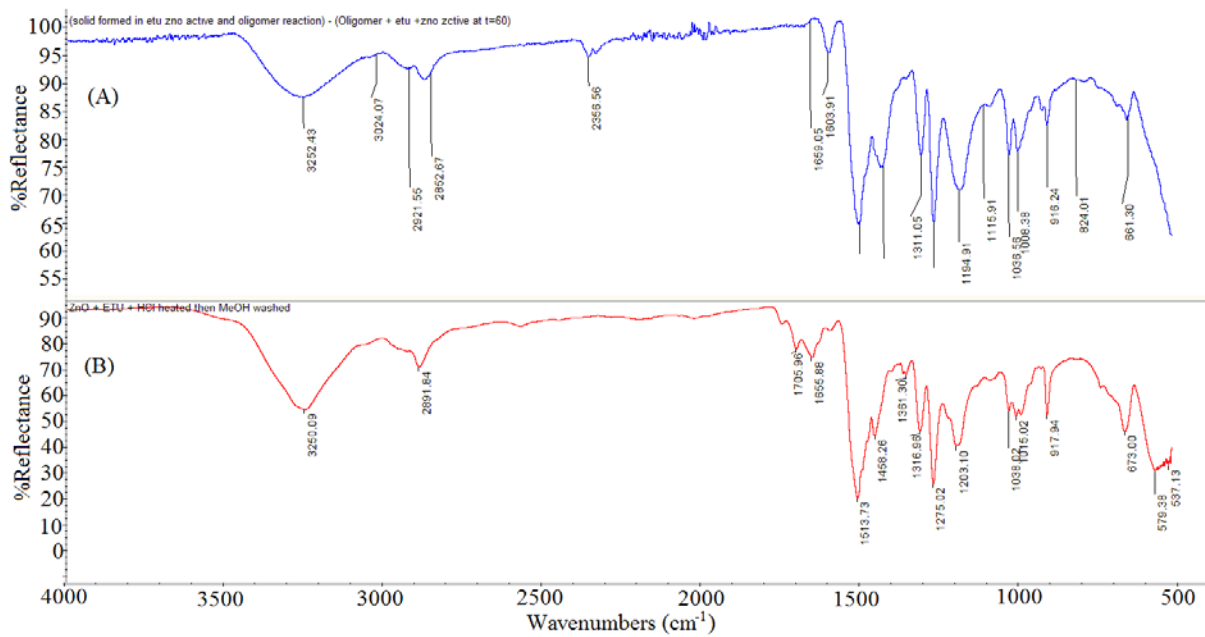


FIGURE 11. FTIR spectra of (A) solid formed in oligochloroprene when heated with ETU and ZnO with the underlying oligomer signal subtracted, and (B) solid formed when ETU, ZnO and HCl are heated, then washed with methanol.

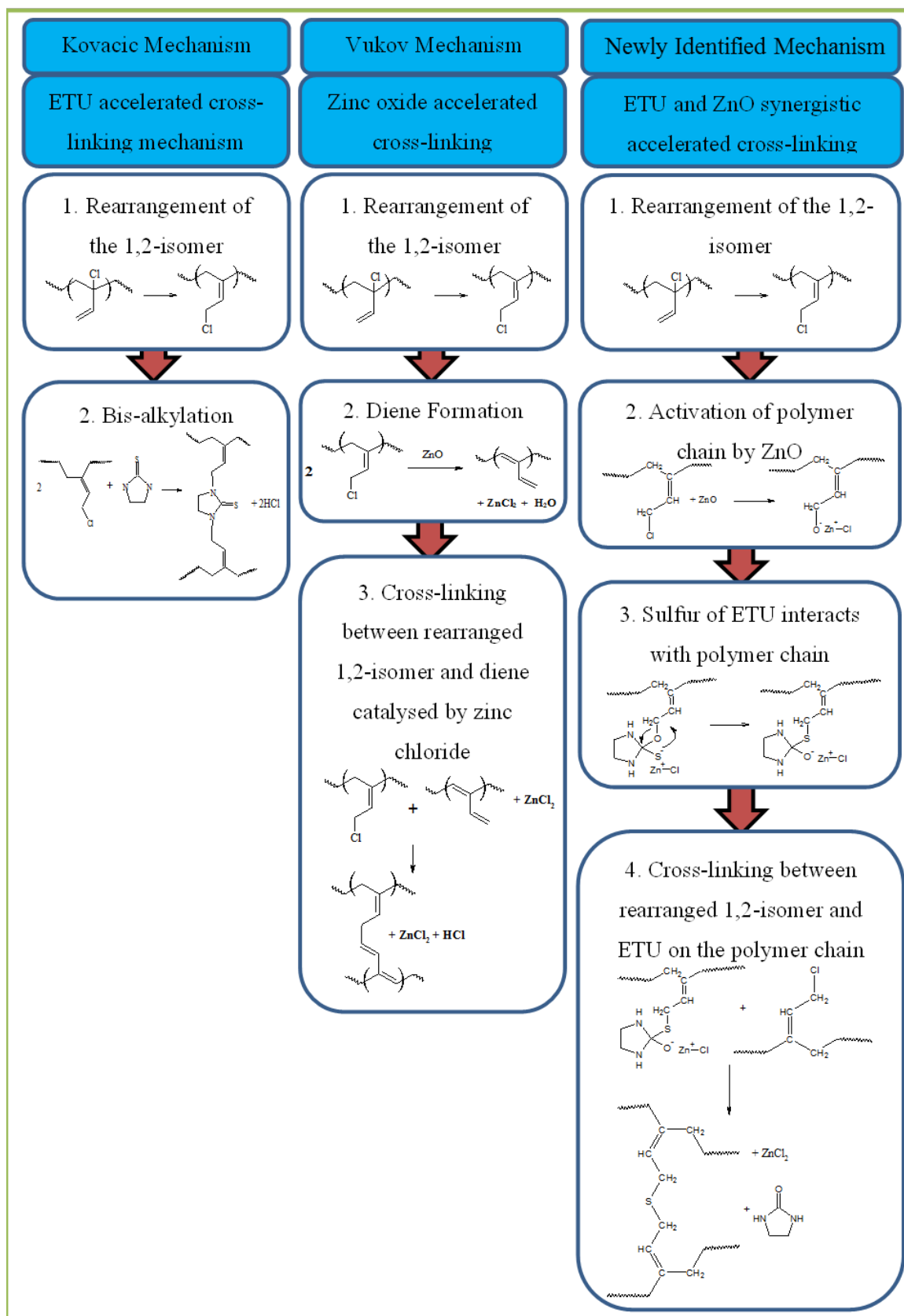
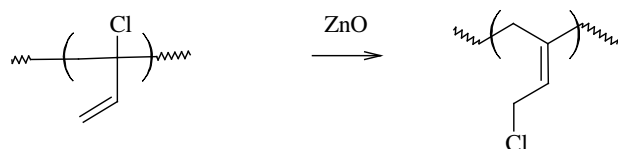
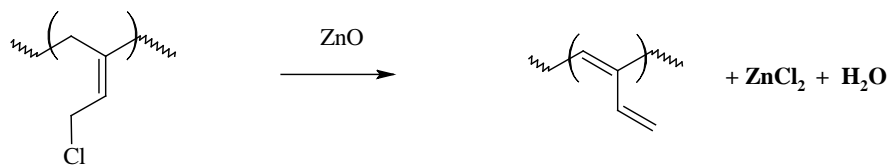


FIGURE 12. Cross-linking mechanisms in effect when ETU and ZnO are present in polychloroprene.

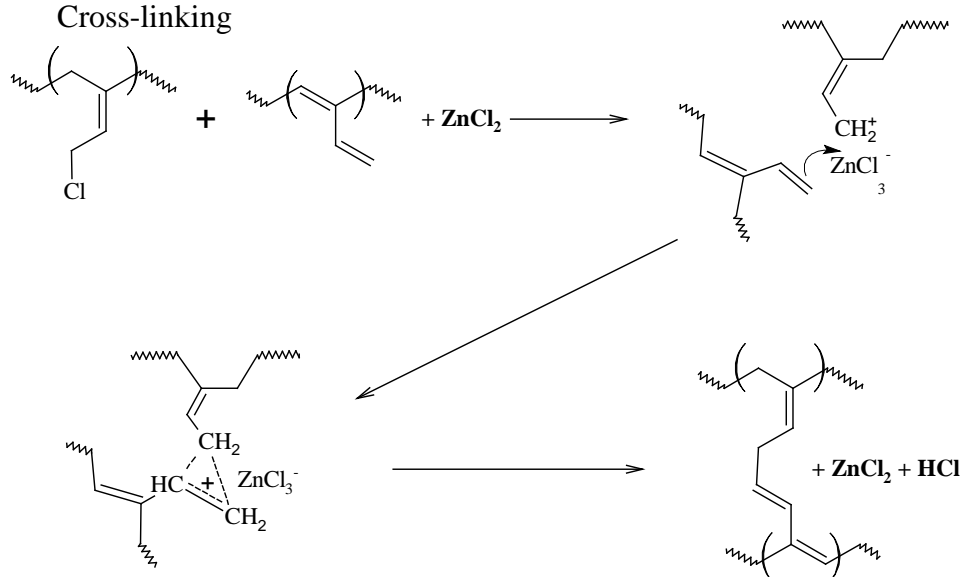
Isomerisation



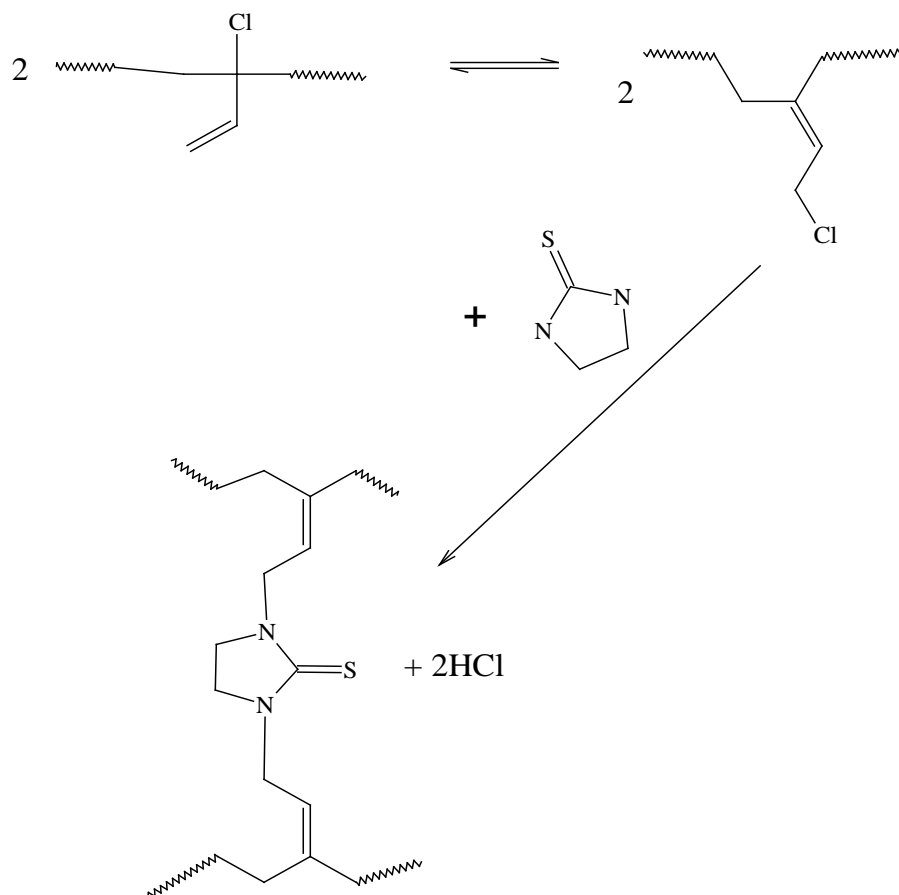
Diene Formation



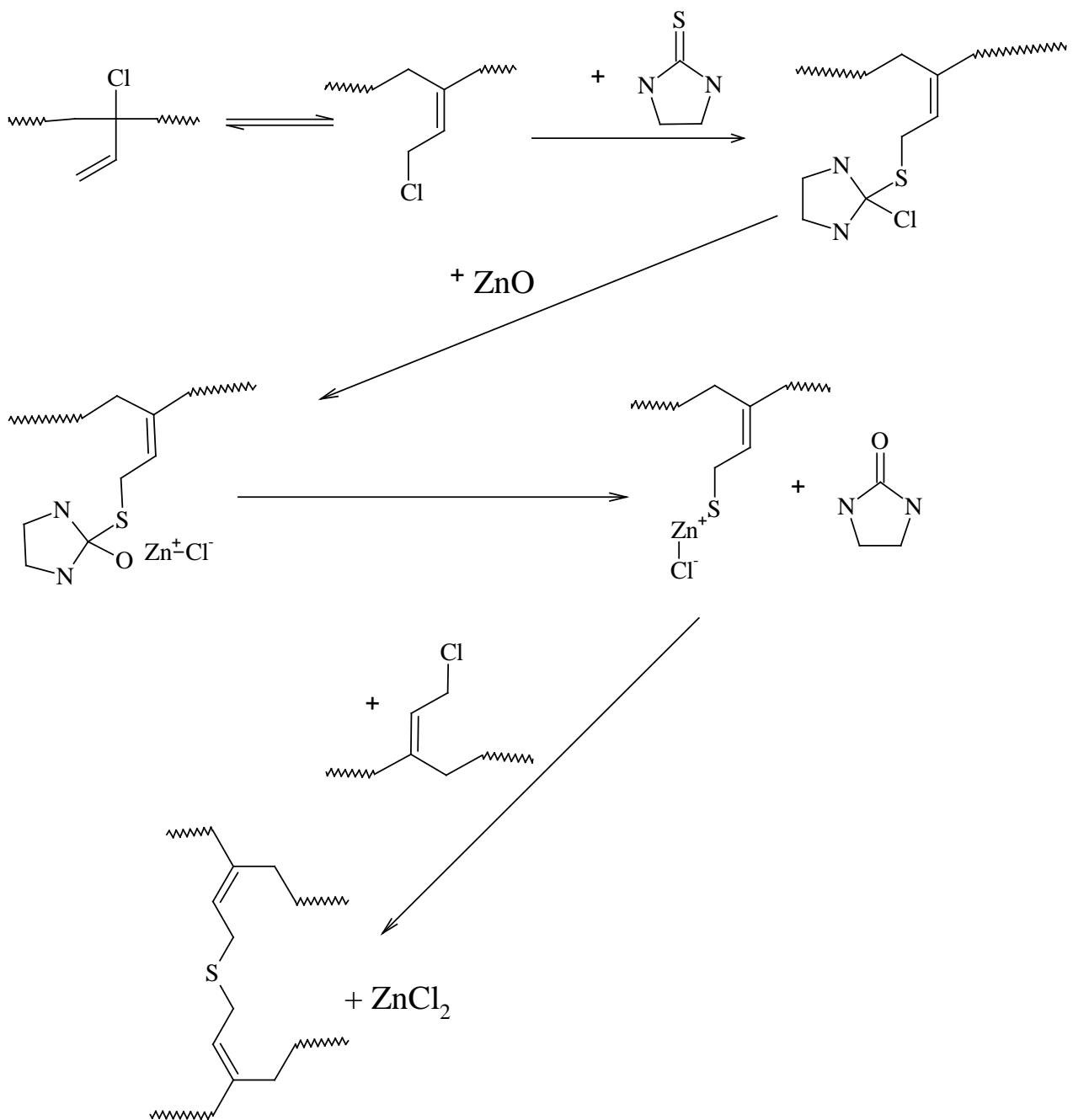
Cross-linking



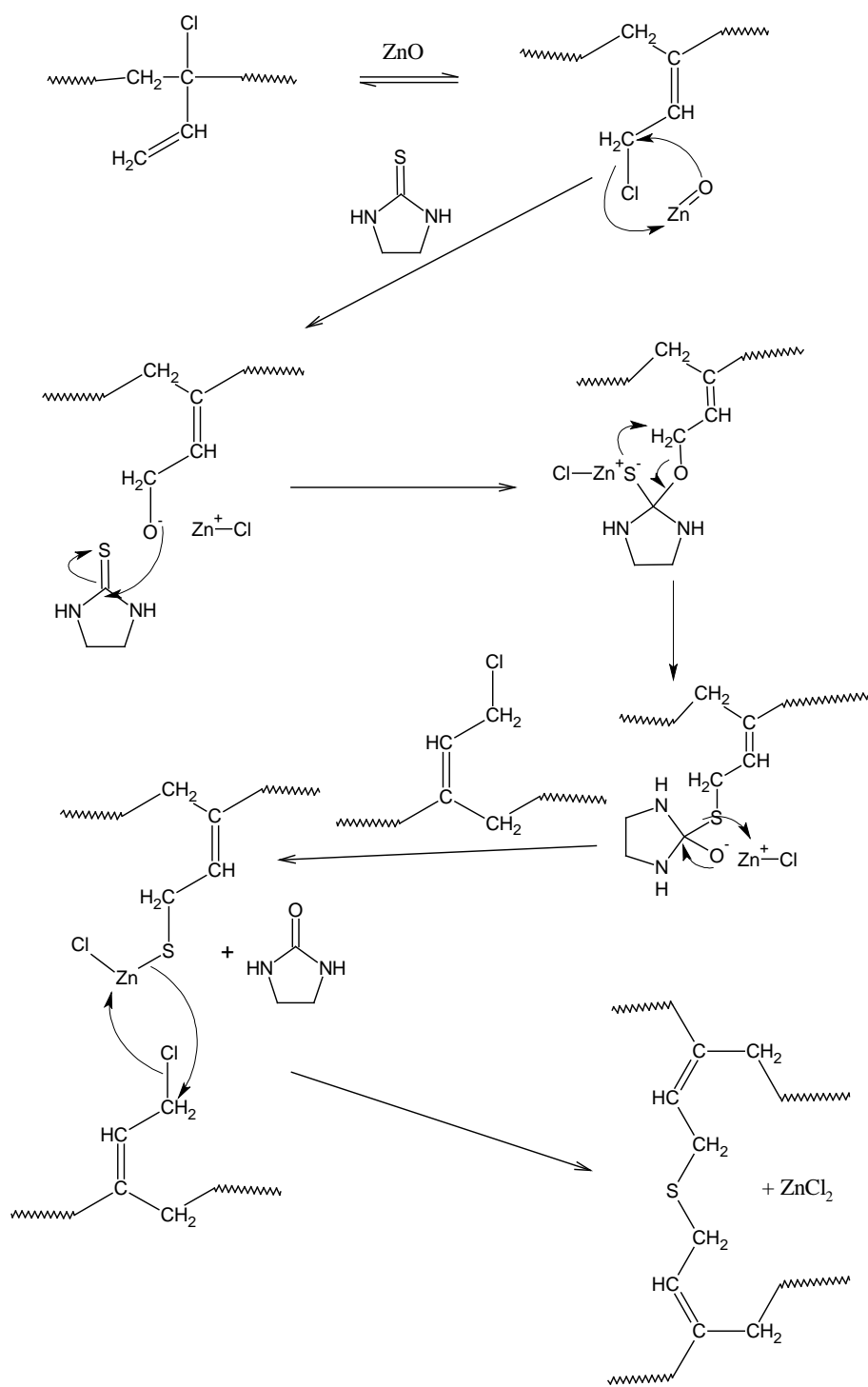
SCHEME 1. Cross-linking mechanism of polychloroprene with ZnO, proposed by Vukov²⁶ using model compounds, shown here with polychloroprene.



SCHEME 2. The bis-alkylation mechanism of Kovacic for the cross-linking of polychloroprene. The mechanism is shown here with ETU, however the original report featured piperazine with magnesium oxide present to quench the hydrochloric acid evolved.



SCHEME 3. Cross-linking mechanism for polychloroprene with zinc oxide and ethylene thiourea working in unison. As first proposed by Pariser.



SCHEME 4. New cross-linking mechanism for polychloroprene with ETU and ZnO, based on the results of the findings herein.

LIST OF FIGURES

FIGURE 1. The four isomeric structures of polychloroprene.

FIGURE 2. FTIR spectra of polychloroprene rubber with 5 phr ZnO, showing (A) uncured ZnO-containing polychloroprene rubber, and (B) after soxhlet extraction. Formation of a new peak at 1580 cm^{-1} is clearly shown.

FIGURE 3. Change in height of the 1580 cm^{-1} peak in polychloroprene with 5 phr ZnO as it cures at $160\text{ }^{\circ}\text{C}$.

FIGURE 4. Change in height of 925 cm^{-1} peak over time for polychloroprene containing ZnO. Note error bars show one standard deviation and are too minor to show above 30 minutes.

FIGURE 5. Chemical structures of model compounds trialed.

FIGURE 6. FTIR spectra of polychloroprene containing 5 phr ETU, (A) before curing and (B) after curing for the region $1400\text{-}1800\text{ cm}^{-1}$. A new peak in the ETU cross-linked sample is shown at $\sim 1550\text{ cm}^{-1}$.

FIGURE 7. Change in the height of 1550 cm^{-1} peak in polychloroprene cured at $160\text{ }^{\circ}\text{C}$ for 30 minutes with 2 phr ETU compared to a rheograph of 2 phr ETU cross-linking polychloroprene at $160\text{ }^{\circ}\text{C}$.

FIGURE 8. FTIR spectra showing new peaks at ~ 1540 and 1580 cm^{-1} when ETU and ZnO are used to cross-link polychloroprene. Spectra are shown from $1400\text{-}1700\text{ cm}^{-1}$ and are translated along the reflectance axis for clarity.

FIGURE 9. Change in height of the 925 cm^{-1} peak in polychloroprene as it cures at $160\text{ }^{\circ}\text{C}$ with ETU and ZnO as additives, compared to ETU or ZnO as separate additives and to pure polychloroprene. Error bars are one standard deviation and are not visible after 30 minutes.

FIGURE 10. FTIR spectra showing (A) methanol soxhlet residue from polychloroprene cured with 2 phr ETU and 5 phr ZnO, and (B) a 1:1 (w/w) mixture of ETU and EU.

FIGURE 11. FTIR spectra of (A) solid formed in oligochloroprene when heated with ETU and ZnO with the underlying oligomer signal subtracted, and (B) solid formed when ETU, ZnO and HCl are heated, then washed with methanol.

FIGURE 12. Cross-linking mechanisms in effect when ETU and ZnO are present in polychloroprene.

LIST OF SCHEMES

SCHEME 1. Cross-linking mechanism of polychloroprene with ZnO, proposed by Vukov²⁶ using model compounds, shown here with polychloroprene.

SCHEME 2. The bis-alkylation mechanism of Kovacic for the cross-linking of polychloroprene. The mechanism is shown here with ETU, however the original report featured piperazine with magnesium oxide present to quench the hydrochloric acid evolved.

SCHEME 3. Cross-linking mechanism for polychloroprene with zinc oxide and ethylene thiourea working in unison. As first proposed by Pariser.

SCHEME 4. New cross-linking mechanism for polychloroprene with ETU and ZnO, based on the results of the findings herein.