Rigid Silicone Resin Studies

by

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Abstract

The motivation of the research was to improve the mechanical integrity of a characteristically brittle, addition silicone resin, while retaining its high heat resistant properties by the incorporation of phase one (I) rubbers such as vinyl terminated PDMS (DP_n=9) and silane terminated rubber (DP_n=4) in its matrix. The modification is being undertaken to develop materials for high temperature composite applications such as those used in high performance aircraft.

The effects of the resin modification by the addition of 0-15% rubber were evaluated by flexural and fracture toughness testing of samples cured with a trifunctional or tetra-functional cross-linker and post-cured under 200°C /4 hour or 260°C/ 8 hour conditions. Other evaluations carried out included Scanning Electron Microscopy (SEM) of fracture surfaces; Dynamic Mechanical Analysis (DMA) and Nuclear Magnetic Resonance (NMR) of selected samples.

The analyses indicated that the 260°C /8 hour post-cure increased the stiffness and fracture toughness of the resin compared to the 200°C /4 hour post-cure, and was the better post-cure condition. The trifunctional cross-linker was able to effect a less brittle matrix than the tetrafunctional cross-linker - evident by higher fracture toughness and fracture energy values.

Solid state ^{29}Si NMR of the resin with the trifunctional cross-linker showed that the full cure was not achieved, possibly because of the dominance of a side reaction: the hydrolysis of the silane groups on the cross-linker which favors the presence of oxygen and water at elevated temperatures. It was found, despite the incomplete extent of resin reaction, the silane terminated rubber additive was better able to increase the fracture toughness and fracture energies on the resin matrix, than the vinyl terminated PDMS. The condition under which the favorable mechanical trends were achieved was a 160°C/16 hour cure with the trifunctional cross-linker, accompanied by a post-cure at 260°C for 8 hours

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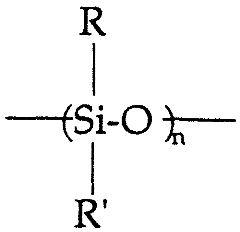
Chapter 1

Introduction

1.1 Silicones and silicone resins

Organosilicon chemistry developed with the conversion of inorganic compounds such as silicon tetrachloride and trichlorosilane to organometallic substances with the general formula $RSiX_3$. These organometallic compounds could, in turn, be hydrolyzed to linear and cyclic siloxanes. It was initially thought that the hydrolysis to create these siloxanes produced double bonded (Si=O) compounds dubbed silicoketones or silicones. It was discovered later via structural analysis that these siloxanes and polysiloxanes possessed Si-O - not - Si=O bonds [1]. However the name '"silicones" remained to define all monomeric and polymeric organic siloxanes, the general structure of silicones is shown in Figure 1.1.



$$-\!\!\left(\overset{\displaystyle R}{\underset{\displaystyle R'}{\overset{|}{\underset{|}{Si}}}}\text{-}O\right)_{\!n}\!\!-$$

Figure 1.1: The general structural formula of silicones

Siloxanes and polysiloxanes are composed of an inorganic siloxane (Si-O) backbone and side groups such as methyl or phenyl groups attached to the silicon. There is relatively free rotation about the siloxane bond due to its length of 1.64 angstroms - larger than the carbon-carbon bond of 1.53 angstroms [2,3,]. This length permits free rotation about the siloxane bond due to the reduced hindrance within the molecule. The energy of rotation about the siloxane bond is ~0 kJ/mol compared to polyethylene carbon-carbon bond rotation energy of ~14kJ/mol [3]. This easy rotation explains the very low glass transition temperatures (T_g) and low melt temperatures (T_m) : e.g. PDMS has a T_g of -125°C and a T_m of -40°C. To further promote the rotational and torsional flexibility, the oxygen atom in the siloxane group possesses no side groups unlike its silicon counterpart; and the Si-O-Si bond of 143° is also larger than a tetrahedral bond of 110° [2]. The high flexibility of the Si-O bond causes the high permeability of siloxanes which is a reason for its use in soft contact lenses, membranous filters and sealants. What is more, the side groups can be changed in order to vary selective permeation of polysiloxane films to small molecules [2,3].

The low intermolecular interaction between side groups such as methyls and phenyls on polysiloxane chains, coupled with its high chain flexibility, causes chains to rearrange so the non-polar methyl or phenyl groups are at the surface or interface. This screens the ionic siloxane backbone resulting in the siloxane chain achieving its lowest energy configuration. It produces the low surface energy and surface tension which are exploited in surfactants and waterproofing materials [2,3]. The low surface energies and flexibility explain the ability of a polysiloxane surface to regenerate its former characteristics, by rotation and rearrangement of the chain, when it is damaged [2]. This property, in addition to its physiological inertness, makes silicones useful in prosthetic devices, implants and other biomedical products [2,4]. The silicon and the oxygen groups on the siloxane backbone demonstrate a very large differentiation in size which gives the chains unique packing characteristics and create unusual compressibility properties [3].

The high oxidation state of the oxygen in siloxane and polysiloxanes causes the partial ionic nature of siloxanes preventing the reduction of the siloxane bonds until very high temperatures (>200°C in air and >500°C in vacuum) [4]. The high dipolar character protects the side groups from chemical attack at temperatures in the 200°C range. It is for this reason that siloxanes are notable for high thermal and oxidative stability. This property has been exploited in such applications as heat transfer agents and high performance elastomers [2,3]. However, pure siloxane polymers are rarely used without modification for technological applications; typically, they are modified by fillers, pigments, copolymerization and curing agents to convert them to useful products, including rubbers and resins [5].

The formation of silicone resins entails the crosslinking of polysiloxanes by the hydrolysis of tri or tetrafunctional chlorosilanes, alkoxysilanes and other reagents in an organic solvent medium. The result is low molecular weight, cross-linked chains with reactive groups still present e.g. silanol or vinyl groups. The condensation reaction with the silanol groups or the addition reaction with the vinyl groups convert these low molecular weight resins to high molecular weight, highly cross-linked, rigid resins[1,3].

Cross-linking can take place in four ways [6]:

- Peroxide-induced free radical reactions.
- Condensation reactions.
- Hydridosilane/silanol reactions.
- Hydrosilylation addition reactions.

Of the four modes of cross-linking, hydrosilylation is the route by which the resin used in this study - Dow Corning X1-2672™- is cross-linked from low molecular weight silicones to a rigid resin. The hydrosilylation is an addition reaction between a silane group and an unsaturated carbon bond. It is enhanced by the presence of a platinum catalyst. The hydrosilylation system is cited by Thomas [6] as one of the most technologically popular reactions because of its simplicity: it releases no byproducts and it requires very minute quantities of catalyst to proceed.

Typically, the hydrosilylation reaction has been used to produce unfilled thin films for the paper and plastics markets, pressure sensitive adhesives and water-based coatings [6]. As far as siloxane polymers are concerned, the hydrosilylation reaction has been investigated for cross-linking PDMS rubbers in the presence of other polymers such as urethanes to form Interpenetrating Polymer Networks (IPNs) [1]. This is because of their low miscibility and unique cross-linking chemistry. Also, most siloxane polymers have inherently low crack resistance and thus need a reinforcing polymer.

The hydrosilylation reaction can be achieved in various ways, but the most popular is the one between a hydridosilane group and a silicon vinyl group [6] shown in Figure 1.2.

$$\equiv \mathrm{Si\text{-}H} + \equiv \mathrm{SiCH{=}CH_2} \xrightarrow{\mathrm{Pt}} \equiv \mathrm{SiCH_2CH_2Si} \equiv$$

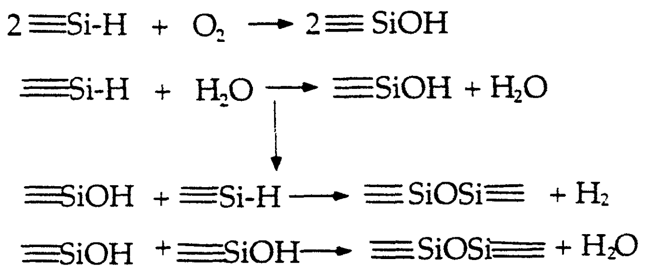
Figure 1.2: The hydrosilylation reaction.

The platinum catalyst used either can be a homogenous or a heterogeneous one. In this investigation homogeneous, hexachloroplatinic acid dissolved in isopropanol formulated by Speier [7], was used. The mechanism for the interaction between this catalyst and the reactants, hypothesized by Chalk and Harrod [8]; and Benkeser and Kang [9], involves the reaction between the platinum and the vinyl group followed by a reaction of the platinum/vinyl intermediate with the silane group to form a complex. The complex then reacts with another vinyl group forming the hydrosilylation cross-link and recycling the catalyst for further reaction.

For a cross-linked network to be formed, the hydrosilylation must take place between reactants, one of which must be multi-functional. The silicone resin used in this study has vinyl groups and the reactant needed to form the resin matrix must be a multi-functional silane molecule. The hydrosilylation cross-linking reaction can produce a variety of matrices depending on the position of the silane groups and the number of the silane functionalities. These reactions are an attractive alternative to peroxide-induced free radical cross-linking because no volatile by-products are formed [2] .

The formation of the three dimensional cross-linked network is achieved by reacting the vinyl group of the silicone with a tri or tetrafunctional silane molecule i.e. a silane cross-linker. The silicone resin used in this study - Dow Corning X1-2672™ - undergoes this hydrosilylation reaction.

However, the hydrosilylation system is vulnerable to side reactions under certain conditions. Upon prolonged heating in air and moisture (e.g. curing in an air oven) oxidation and hydrolysis of the silane groups can take place [6]. This becomes even more significant if the silane groups are present in excess. It was shown by Quan [10] that the presence of the excess silane groups could react with air and moisture to produce silanols or silsesquioxane cross-links shown in Figure 1.3. These reactions cause changes in the resin network which include lower stiffness due to lower cross-link density and different types of cross-links than those produced by the primary reaction.



$$2\equiv\mathrm{Si\text{-}H} + O_2 \longrightarrow 2\equiv\mathrm{SiOH}$$

$$\equiv\mathrm{Si\text{-}H} + H_2O \longrightarrow \equiv\mathrm{SiOH} + H_2O$$

$$\equiv\mathrm{SiOH} + \equiv\mathrm{Si\text{-}H} \longrightarrow \equiv\mathrm{SiOSi}\equiv + H_2$$

$$\equiv\mathrm{SiOH} + \equiv\mathrm{SiOH} \longrightarrow \equiv\mathrm{SiOSi}\equiv + H_2O$$

Figure 1.3: The side reactions of hydrosilylation cross-linking.

Silicone resins have had relatively little use in composites, despite their uses in other applications. Instead, they have mainly been used to modify other resins, such as urethanes, epoxies and acrylates; as copolymers with polyimides to improve moisture resistance; as a reactant with caprolactam to improve the low temperature properties of the polyimide product; and as comonomers in the formation of siloxane block copolymers [3].

The reason for the small use in composites is their brittleness. The resins are stable at high temperatures and can withstand temperature extremes without loss of integrity. It is because of this that they would be desirable for composites in applications such as engine casings for high performance aircraft [11]. To reduce the brittleness while maintaining the heat stability, the resins are being modified with rubber, which makes them tougher.

Current efforts are focused on incorporating the rubber directly into the resin network via addition or condensation reactions. These are called Phase I rubbers and when properly incorporated into the network, they induce localized plastic flow, if cracks develop and propagate in the resin [11]. Thus the network is more impact and crack resistant, while retaining its high temperature stability, good stiffness and strength.

When phase I modification is achieved, then larger, discrete Phase II rubber particles will be formed in the resin network. These will further toughen the resin, increasing its fracture toughness and fracture energy by a number of mechanisms [12].

Fracture Toughness (K_C), defined as the critical stress intensity factor, measures a material's resistance to crack initiation. K_C is related to the stress (σ) and the critical length (a), at which a crack will begin to propagate in an unstable manner, by Equation (1):

$$K_c = \sigma\,(\pi \times a)^{1/2} \tag{1}$$

The work required to fracture the material is the Fracture Energy (G_C). G_C measures the resistance of a material to crack propagation and is related to K_C by equation (2) below:

$$G_c = K_c^2 / E \tag{2}$$

E is the modulus of the material.

Fracture Toughness can be measured in three modes:

- Mode I - fracture by crack opening
- Mode II - fracture by shear
- Mode III - fracture by tearing

Mode I Fracture Toughness (K_{IC}) and Fracture Energy (G_{IC}) are the parameters that were measured and discussed in this investigation.

Polymers exhibit fracture mechanisms which are different from metals and ceramics due to the absence of crystallographic planes, dislocations and grain boundaries. Polymers, composed of long molecular chains, exhibit mechanisms that involve the rupture of the covalent bonds between the atoms and the breakage of Van der Waals bonds between the molecules. In cross-linked, glassy polymer Van Der Waals bond breakage is minimal. These materials yield and fail by breakage of the covalent bonds. For all glassy polymers, the Van Der Waals bonds can play a significant role in deformation and yield processes while ultimate fracture involves covalent bond breakage [13].

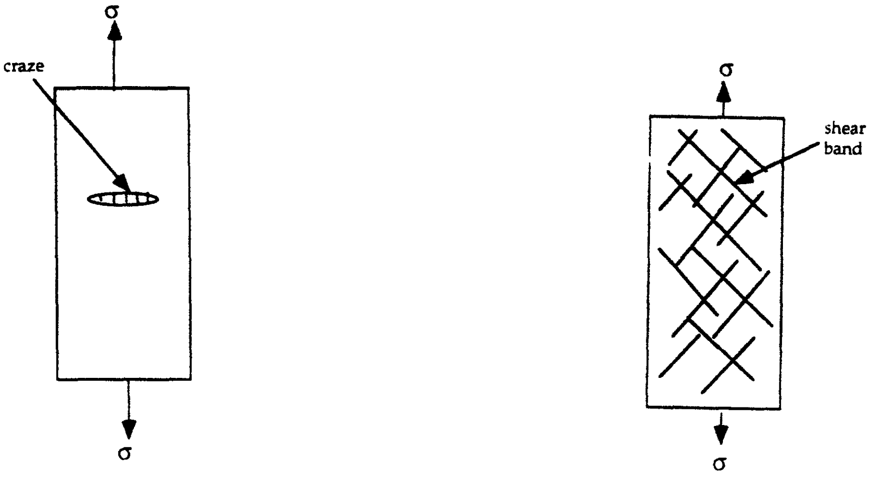
Yielding in polymers can take place by three mechanisms:

- Crazing
- Shear Banding
- Shear Yielding

Crazing is a localized, inhomogeneous deformation that results from the application of a tensile stress. This causes the polymer molecules to orient parallel to the tensile direction. With higher deformation, microvoids develop between the oriented chains with fibrils of polymer connecting the opposite surfaces of the voids. Stresses are concentrated in the fibrils and cause the growth of the craze. As a result, ultimate fracture follows the rupture of the fibrils [13-14].

Shear Banding is another mode of local deformation which is characterized by chain orientation under a shear stress. Unlike crazing however, microvoids do not form; instead bands of oriented polymer develop at an angle to the tensile axis [13-15].

Craze and shear band structures are shown in Figure 1.4 (a) and (b) respectively. These two phenomena occur in glassy amorphous thermoplastics such as polystyrene and polymethylmethacrylate.



(a)

(b)

Figure 1.4: (a) Structure of a craze and (b) structure of shear bands formed in thermoplastic polymers.

Shear Yielding shown in Figure 1.5 is global deformation which results in the orientation of polymer chains throughout the specimen due to the imposition of a critical shear stress. Typically, shear yielding is favored over crazing and shear banding when the crystallinity of a polymer increases [13].

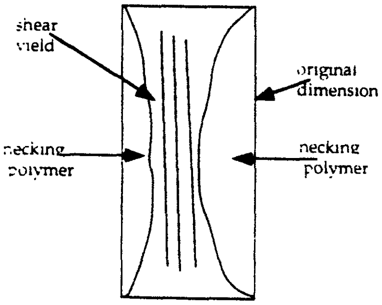


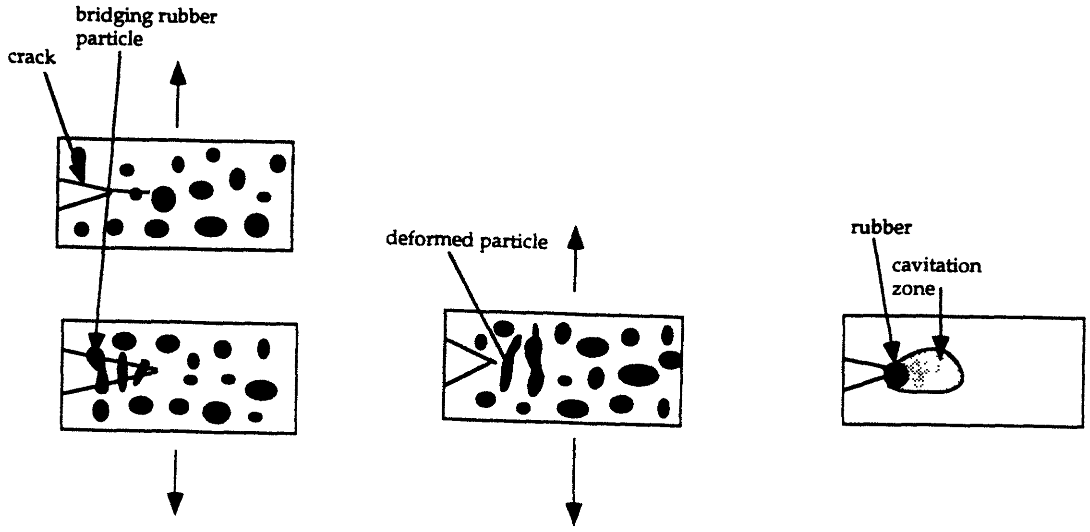
Figure 1.5: Shear Yielding in a Polymer.

According to Bradley et al, for thermoset resins there is little evidence that crazing and shear banding occur. The cross-links prevent the formation of crazes and shear bands so the molecules are unable to orient. However, some deformation can take place by shear yielding. This is characterized as 'diffuse' because only small deformation zones can be formed. Fracture in thermoset resins occurs as a result of covalent bond breakage; the magnitude of the stress required increases as the cross-link density increases [17,18].

Rubber modified thermoset resins are toughened by three possible mechanisms [12,19,20]: crack bridging of rubber particles, impeding the advance and opening of a crack; increased deformation of the rubber particle and its surrounding matrix; and by cavitation of the rubber particle causing more localized shear yielding in the matrix.

Matrix shear yielding is cited as the most effective energy dissipating mechanism [12] and it is desired that this will take place when the silicone resin is modified. It should be evident from the presence of localized deformation zones, and cavitated rubber particles in the matrix a change from brittle to ductile fracture.

Figure 1.6 (a), (b) and (c) show crack bridging; deformation of rubber particles in the matrix and particle cavitation, along with localized shear yielding.



(a) (b) (c)

Figure 1.6: (a) crack bridging (b) rubber particle deformation (c) rubber particle cavitation and localized shear yielding.

1.2 Modification of Dow Corning X1-2672™ resin

The silicone resin Dow Corning X1-2672™ has the following structural formula shown in Figure 1.7.

$$(\mathrm{PhSiO_{3/2}})_{0.75}(\mathrm{Me_2ViSiO_{1/2}})_{0.25}$$

Ph = Phenyl group
Me = Methyl group
Vi = Vinyl group

Figure 1.7: The structural formula of Dow Corning X1-2672™.

X1-2672™ is a clear, colorless fluid which has the consistency of a syrup. It possesses vinyl functionality and for this reason it is necessary for its cross-linker to have silane functionalities to produce the three dimensional network via hydrosilylation. The cross-linkers used in this study were tri-functional and a tetra-functional. The tri-functional cross-linker is phenyltris(dimethylsiloxy)silane, shown in Figure 1.8.

$$\mathrm{PhSi(OSiMe_2H)_3}$$

Ph = Phenyl group
Me = Methyl group
Vi = Vinyl group

Figure 1.8: The structural formula for phenyltris(dimethylsiloxy)silane.

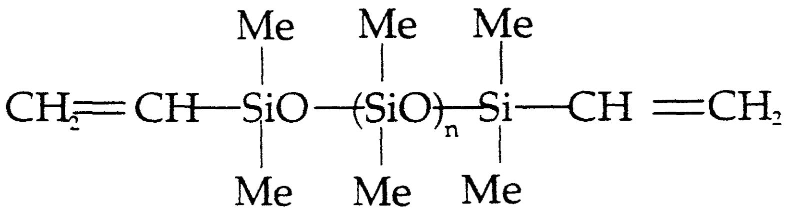
The tetra-functional cross-linker used was tetrakis(dimethylsiloxy)silane, shown in Figure 1.9.

$$Si(OSiMe_2H)_4$$

Me = Methyl group

Figure 1.9: The structural formula of tetrakis(dimethylsiloxy)silane.

Two short chain oligomers were investigated for incorporation into the X1-2672™ matrix as Phase I rubbers. The first rubber was a vinyl terminated PDMS with an average degree of polymerization (DP_n) of 9. The general formula is shown in Figure 1.10.

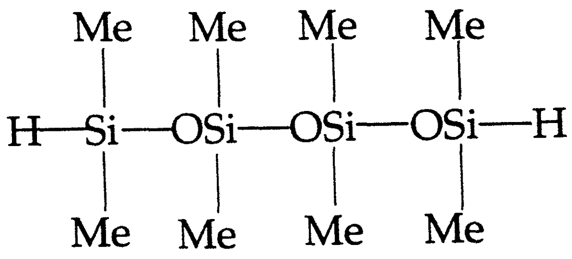


$$CH_2{=}CH{-}\overset{Me}{\underset{Me}{Si}}O{-}(\overset{Me}{\underset{Me}{Si}}O)_n{-}\overset{Me}{\underset{Me}{Si}}{-}CH{=}CH_2$$

Me = Methyl group

Figure 1.10: The general formula of vinyl terminated PDMS with a DP_n of 9.

The second Phase I rubber used in this investigation was 1,1,3,3,5,5,7,7 octamethyltetrasiloxane - a silane terminated rubber - with an average degree of polymerization of 4. The formula is shown in Figure 1.11.



$$H-\underset{Me}{\overset{Me}{Si}}-O\underset{Me}{\overset{Me}{Si}}-O\underset{Me}{\overset{Me}{Si}}-O\underset{Me}{\overset{Me}{Si}}-H$$

Me = Methyl group

Figure 1.11: The formula of 1,1,3,3,5,5,7,7, octamethyltetrasiloxane with a DP_n of 4.

The vinyl terminated PDMS was incorporated into the matrix via reaction with the cross-linkers because it possesses vinyl functionalities and, as a result, cannot react directly with the resin. The silane terminated rubber was incorporated into the network by reaction with the vinyl groups on the X1-2672™ resin. The silane terminated rubber cannot react directly with the cross-linkers and stoichiometrically, the resin will require less cross-linker as more silane terminated rubber is added due to the same functionality possessed by both rubber and cross-linker.

Chapter 2

Experimental

2.1 Sample Preparation.

The process of casting preparation is shown in Figure 2.1 below.

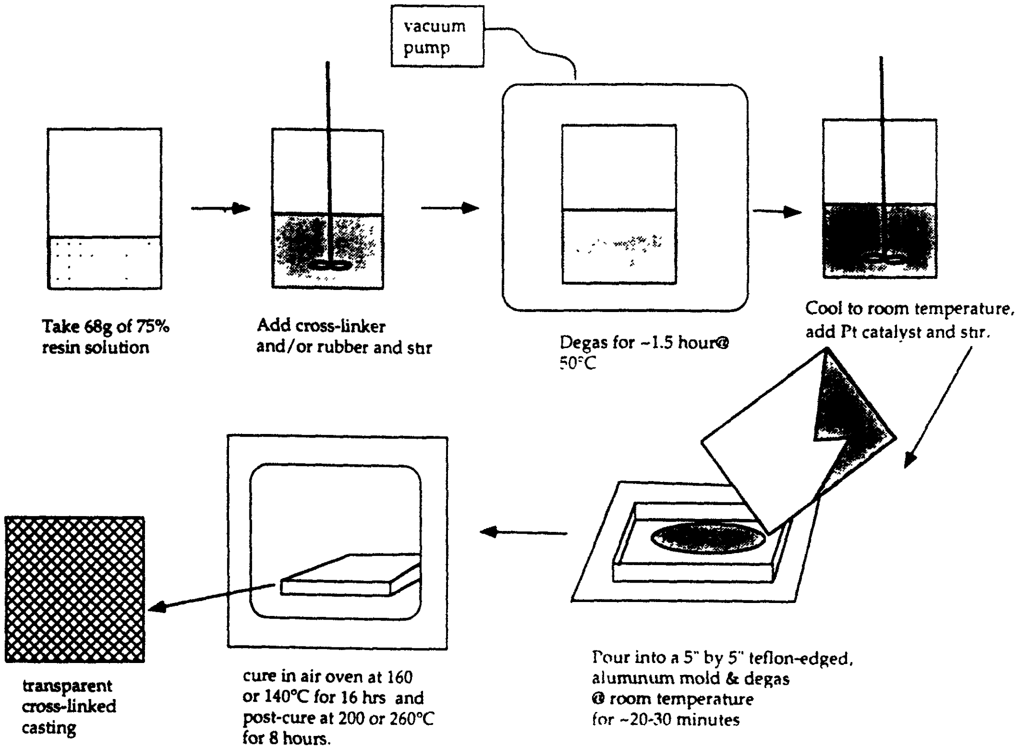


Figure 2.1: Process of making X1-2672™ resin castings

For the preparation of the neat resin casting, 68 grams of a 75% solution of Dow Corning X1-2672™ in toluene was mixed with 11.62 grams of the trifunctional cross-linker phenyltris(dimethylsiloxy)silane purchased from United Chemical Technologies (~95% pure). The two reactants were stirred in a beaker and then degassed under vacuum at 50°C for approximately 1.5 hours in order to remove the toluene. The mixture was then cooled to room temperature, following which 1.5 mL of a 4.0×10^{-3} molar stock solution of hexachloroplatinic acid (Aldrich Chemical Company) in isopropanol (spectrophotometric grade, Mallinckredt Chemical Incorporated) was added as the catalyst. The mixture was stirred and poured in a mold made of an aluminum base and teflon edges approximately 5" x 5"x 1/2" in dimension and degassed again under vacuum at room temperature. The casting was then cured at 160°C for 16 hours and post-cured at 200 or 260°C for 4 or 8 hours respectively. The resulting castings were transparent with a thickness of about 0.3".

The quantities of cross-linker required varied with the amount of rubber added. The first rubber used, vinyl terminated PDMS, was purchased from Gelest (~95% pure) and the second rubber 1,1,3,3,5,5,7,7 octamethyltetrasiloxane (~95% pure) was purchased from Untied Chemical Technologies. The purity of both rubbers was determined from ^{29}Si NMR analysis. The formulations for the rubber addition are shown in Appendices A-1 & A-2:

Resin castings also were made with the tetrafunctional cross-linker tetrakis(dimethylsiloxy)silane (~95% pure) purchased from United Chemical Technologies. The mixing and degassing procedure was the same as that for the trifunctional cross-linker, however, because of the higher cross-link functionality, the cure schedule had to incorporate a slow ramp to a lower cure temperature of 140°C to avoid the extensive cracking of the castings. The formulations for making these castings with the two rubber additives are shown in Appendices A-3 & A-4 and the ramp schedule used to make the casting with the tetrafunctional cross-linker is shown in Figure A-5.

The following castings were made with the rubber percentages being calculated by weight of the neat resin:

- X1-2672™ with 0,3,6 and 9% vinyl terminated PDMS, cured with the trifunctional cross-linker at 160°C for 16 hours and post-cured at 200°C for 4 hours.
- X1-2672™ with 0,3,6 and 9% silane terminated rubber cured with the trifunctional cross-linker at 160°C for 16 hours and post-cured at 200°C for 4 hours.
- X1-2672™ with 0,3,6,9,12 and 15% vinyl terminated PDMS, cured with the trifunctional cross-linker at 160°C for 16 hours and post-cured at 260°C for 8 hours.
- X1-2672™ with 0,3,6,9,12 and 15% silane terminated rubber, cured with the trifunctional cross-linker at 160°C for 16 hours and post-cured at 260°C for 8 hours.
- X1-2672™ with 0,3,6 and 9% vinyl terminated PDMS, cured with the tetrafunctional cross-linker at 140°C for 16 hours and post-cured at 260°C for 8 hours.
- X1-2672™ with 0,3,6 and 9% silane terminated rubber, cured with the tetrafunctional cross- linker at 140°C for 16 hours and post-cured at 260°C for 8 hours.

2.2 Mechanical Testing.

2.2.1 Three-point Bend Testing

All samples were tested in flexure in accordance with ASTM standard D790 on an Instron. The test samples were 2.0 inches in length, 0.5 inch wide and 0.125 inch thick. The samples were cut from the castings, polished and then left for 24 hours at room temperature before being tested on supports with a span of 1.5 inches at a cross-head rate of 0.04 inch/minute. The following parameters were measured:

- Flexural Modulus (E)
- Flexural Stress or Strength at Yield (σ)
- Yield Strain (ε)
- Toughness or Energy derived from the integral of the load-displacement curve

2.2.2 Fracture Toughness Testing

All samples were tested in bending for fracture toughness properties. The samples were tested in accordance with ASTM standard D5045. The samples had a single edge notch of 0.01 inch and were pre-cracked with a razor blade to eliminate the energy required to initiate the crack. The sample dimensions were 2 inches in length, 0.375 inch in width and 0.125 inch thick. The samples were cut from the castings, polished and conditioned for 24 hours at room temperature, before being tested at a cross-head rate of 0.04 inch/minute between supports with a span of 1.5 inches. The following parameters were measured:

- Mode I Fracture Toughness K_{IC}
- Mode I Fracture Energy G_{IC}

2.3 Scanning Electron Microscopy (SEM)

Following fracture toughness testing, the fractured samples were examined with SEM. This was done to establish the mode of fracture. All samples underwent microscopy, but only the following are shown in Chapter 3:

- X1-2672™ neat cured with the trifunctional cross-linker at 160°C for 16 hours and post-cured at 260°C for 8 hours.
- X1-2672™ with 6% vinyl terminated PDMS cured with the trifunctional cross-linker at 160°C for 16 hours and post-cured at 260°C for 8 hours.
- X1-2672™ with 6% silane terminated rubber cured with the trifunctional cross-linker at 160°C for 16 hours and post-cured at 260°C for 8 hours.
- X1-2672™ neat cured with the tetrafunctional cross-linker at 140°C for 16 hours and post-cured at 260°C for 8 hours.
- X1-2672™ with 6% vinyl terminated PDMS cured with the tetrafunctional cross-linker at 140°C for 16 hours and post-cured at 260°C for 8 hours.
- X1-2672™ with 6% silane terminated rubber cured with the tetrafunctional cross-linker at 140°C for 16 hours and post-cured at 260°C for 8 hours.

2.4 Nuclear Magnetic Resonance (NMR)

^{29}Si solid state NMR was carried out at Dow Corning Corporation on the following samples in order to establish the amount of reactive groups present after cure:

- X1-2672™ neat cured with trifunctional cross-linker at 160°C for 16 hours and post-cured at 260°C for 8 hours.
- X1-2672™ with 9% vinyl terminated PDMS cured with the trifunctional cross-linker at 160°C for 16 hours and post-cured at a temperature of 260°C for 8 hours.
- X1-2672™ with 9% silane terminated rubber cured with the trifunctional cross-linker at 160°C for 16 hours and post-cured at a temperature of 260°C for 8 hours.

2.5 Dynamic Mechanical Analysis (DMA).

The following samples were analyzed for their viscoelastic response under an oscillatory tensile load[21] using a Seiko DMS200 Dynamic Mechanical Spectrometer. Each sample placed in the instrument had average dimensions of 4 mm width, 0.7 mm thickness and a gauge length of 15 mm. An oscillatory tensile stress was applied at a frequency of 5 Hertz and an amplitude of 30 micron while undergoing a temperature ramp from -150°C to +300°C at a rate of 2°C per minute. The following samples underwent DMA:

- X1-2672™ neat cured with the trifunctional cross-linker at 160°C for 16 hours and post-cured at 260°C for 8 hours.
- X1-2672™ with 6 and 12% vinyl terminated PDMS, cured with the trifunctional cross-linker at 160°C for 16 hours and post-cured at 260°C for 8 hours.
- X1-2672™ with 6 and 12% silane terminated PDMS, cured with the trifunctional cross-linker at 160°C for 16 hours and post-cured at 260°C for 8 hours.

Chapter 3

Results

3.1 Mechanical Testing

3.1.1 Effect of post-cure temperature and time for X1-2672™ castings with vinyl and silane terminated rubbers.

For the castings that were post-cured at 200°C for 4 hours, all the solutions from which they were made were clear up to 9% rubber content. All the castings were transparent and colorless after undergoing the first cure step at 160°C. After the post-cure at 200°C/4 hours the castings were still transparent but slightly yellow, indicating some degradation of the resin. The castings were flexible when tested by hand. Since these resins felt as if they had not been fully post-cured, the post-cure temperature and time were increased to 260°C and 8 hours. The castings that were made with the increased post-cure temperature and time were made from solutions which were clear and colorless up to 15% rubber content. After the post-cure, the castings were still transparent but they were a darker yellow than those post-cured at 200°C/4 hours and they were harder to bend by hand.

Three point bend testing and fracture toughness tests were used to measure the effect of post-cure temperature and time on X1-2672™ castings. Figures 3.1-3.12 show the mechanical properties and the variation of average values with rubber content of X1-2672™ with 0,3,6, and 9% vinyl terminated PDMS post-cured at 200°C for 4 hours and those samples post-cured at 260°C for 8 hours. The values for an unpost-cured casting are also included as the control and these values show that both post-cures produced a higher extent of cure. The values for the unpost-cured sample are shown only in the graphs with the samples containing vinyl terminated PDMS but these values can be compared with all post-cured samples tested. Figures 3.13-3.24 show the comparison of mechanical properties and the variation of average values with rubber content for X1-2672™ with 0,3,6, and 9% silane terminated rubber. All samples were cured with the trifunctional cross-linker. The flexural testing and fracture toughness data are presented in Appendices B-1 to B-12.

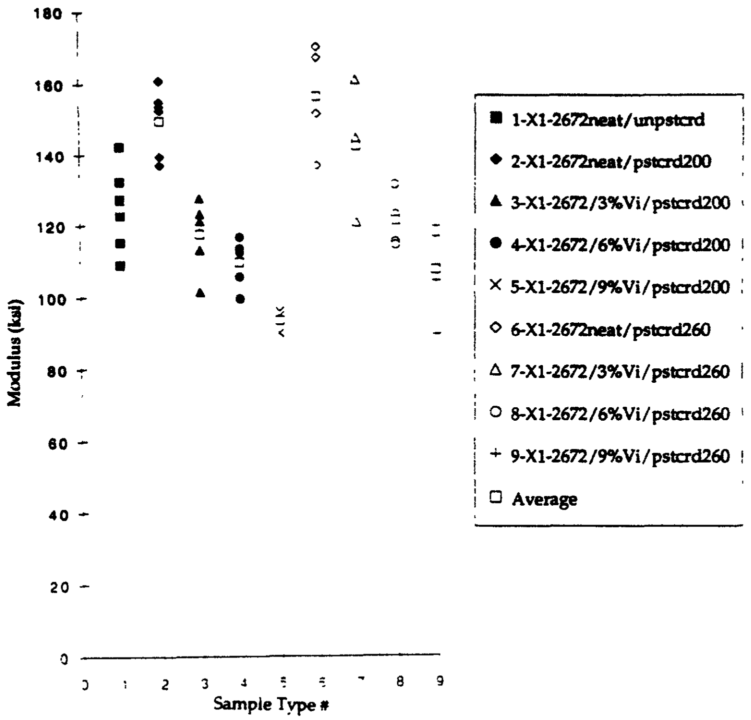


Figure 3.1: The flexural modulus of X1-2672™ castings with vinyl terminated PDMS (DP_n=9), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

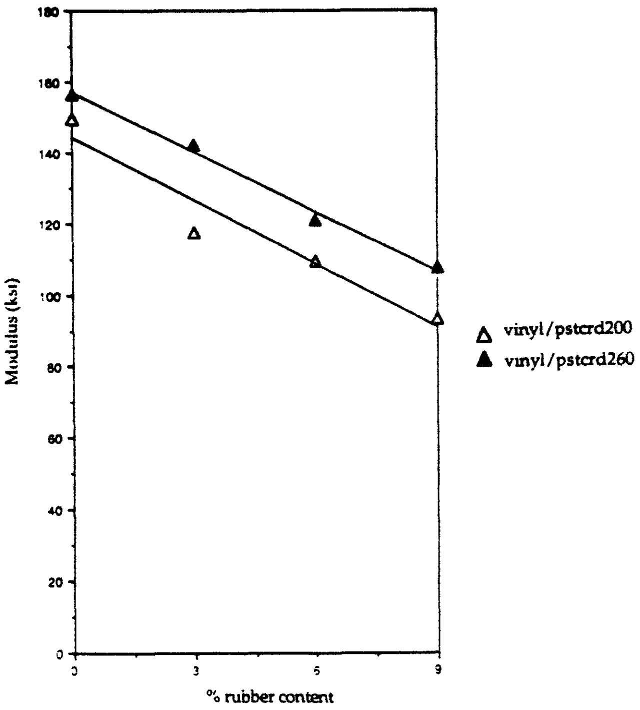


Figure 3.2: Variation of the average flexural modulus with rubber content for X1-2672™ castings with vinyl terminated PDMS (DP_n=9), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

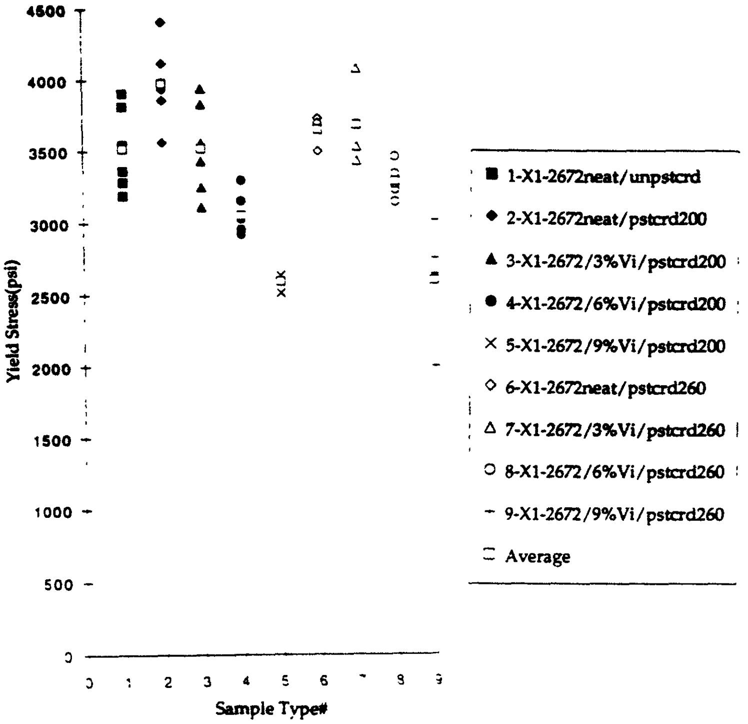


Figure 3.3: The flexural strength of X1-2672™ castings with vinyl terminated PDMS (DP_n=9), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

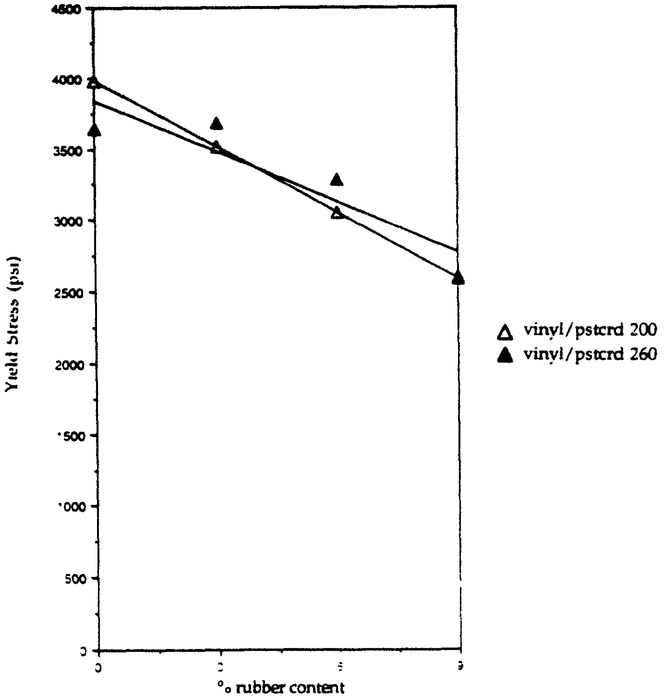


Figure 3.4: Variation of the average flexural strength with rubber content for X1-2672™ castings with vinyl terminated PDMS (DP_n=9), post-cured at 200°C /4 hours and 260°C /8 hours. All samples were cured with the trifunctional cross-linker.

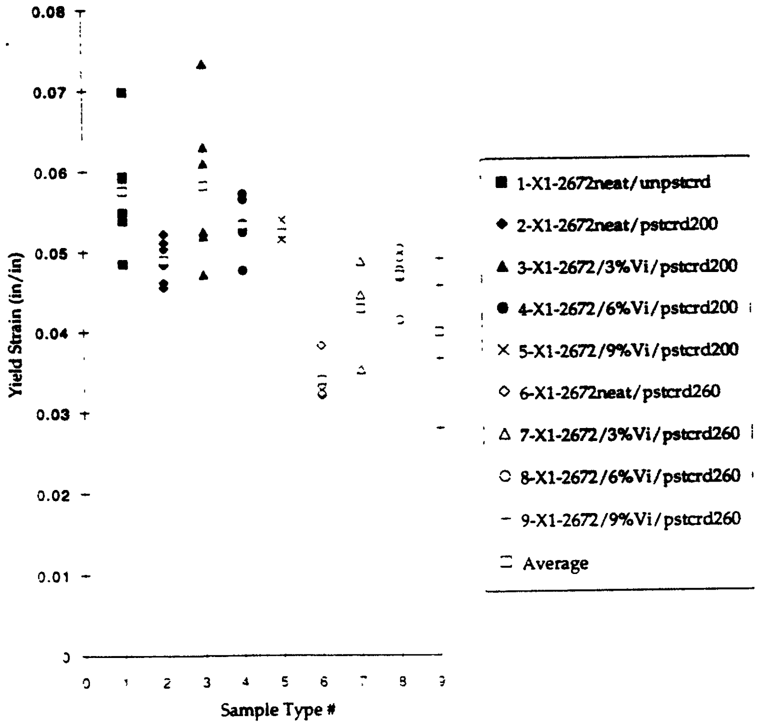


Figure 3.5: The yield strain of X1-2672™ castings with vinyl terminated PDMS (DP_n=9), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

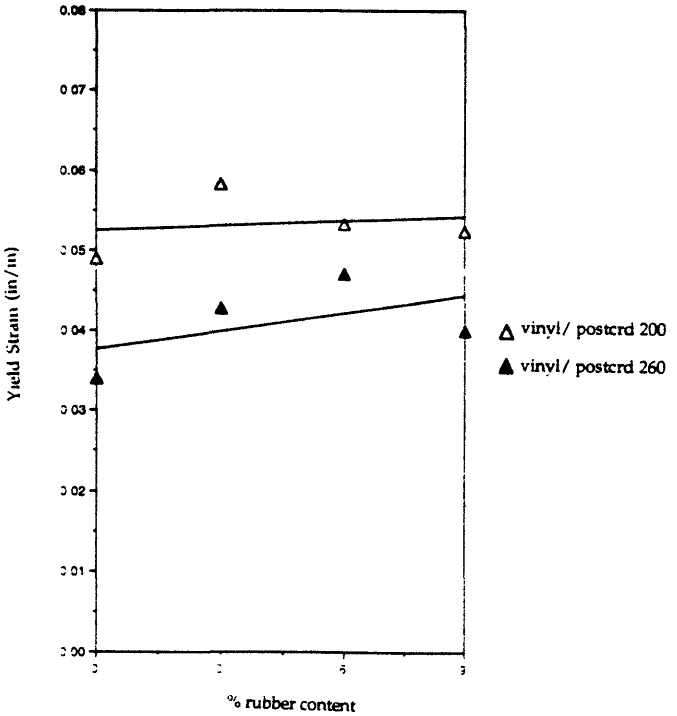


Figure 3.6: Variation of the average yield strain with rubber content for X1-2672™ castings with vinyl terminated PDMS (DP_n=9), post-cured at 200°C /4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

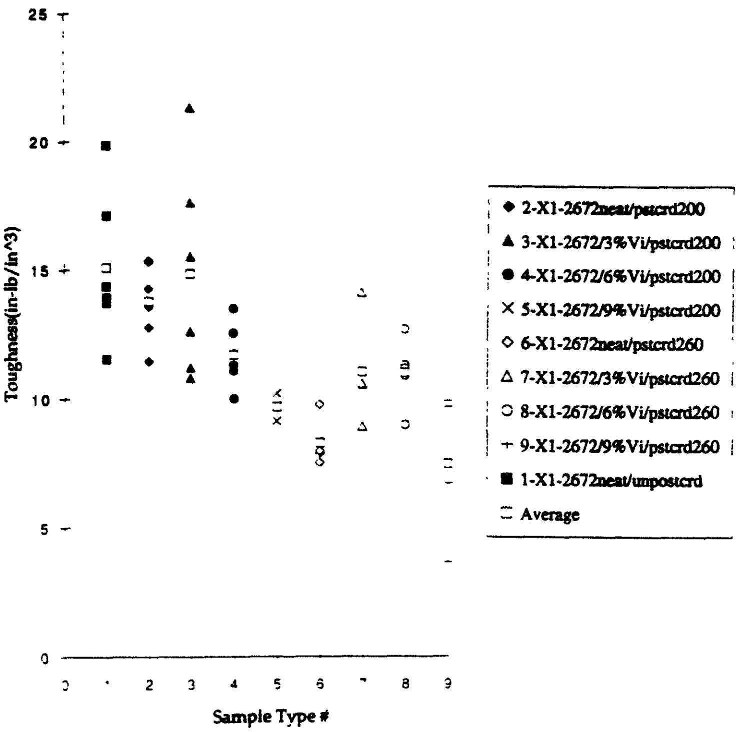


Figure 3.7: Toughness (load-displacement integral) of X1-2672™ castings with vinyl terminated PDMS (DP_n=9), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

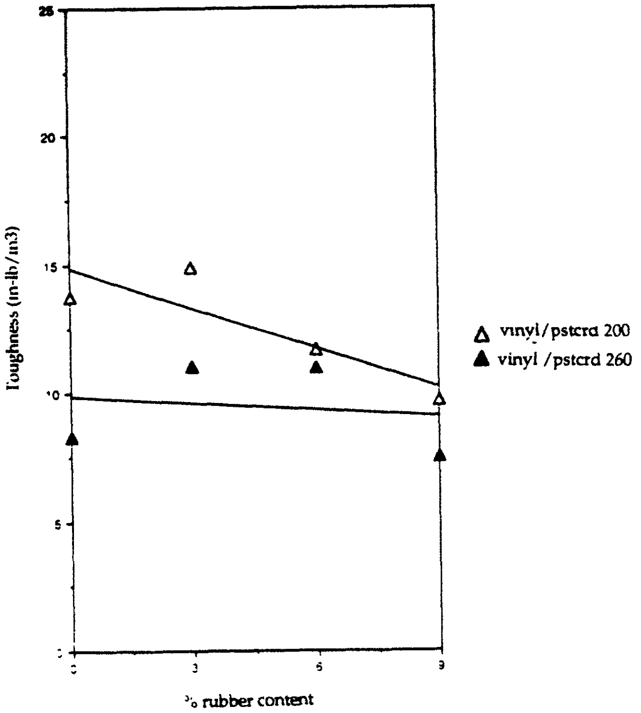


Figure 3.8: Variation of the average toughness (load-displacement integral) with rubber content for X1-2672™ castings with vinyl terminated PDMS (DP_n=9), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

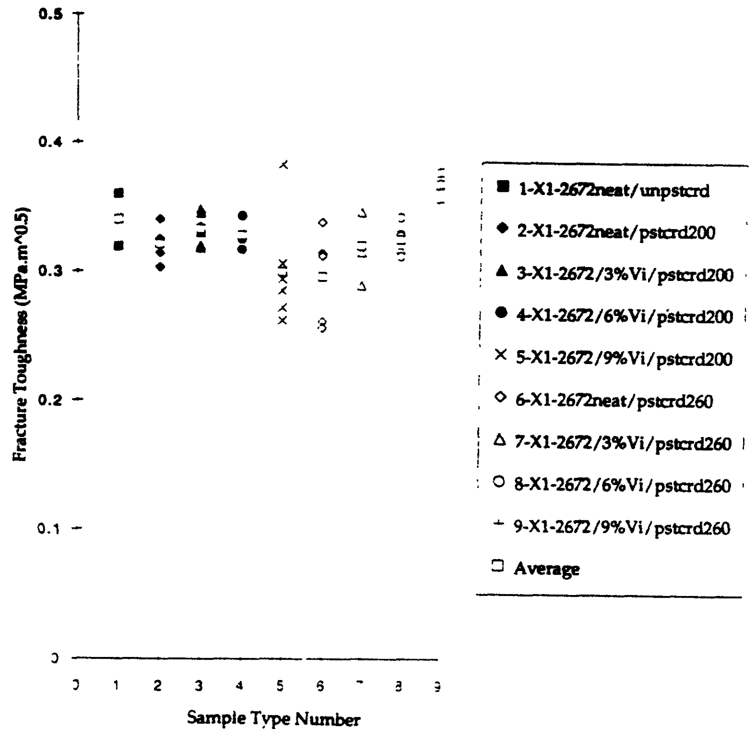


Figure 3.9: The fracture toughness (K_{IC}) of X1-2672™ castings with vinyl terminated PDMS (DP_n=9), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

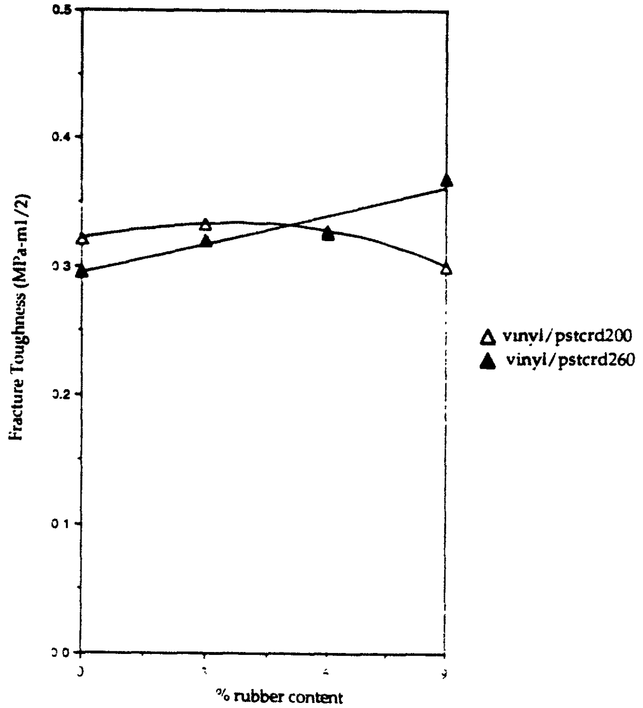


Figure 3.10: Variation of the average fracture toughness (K_{IC}) with rubber content for X1-2672™ castings with vinyl terminated PDMS (DP_n=9), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

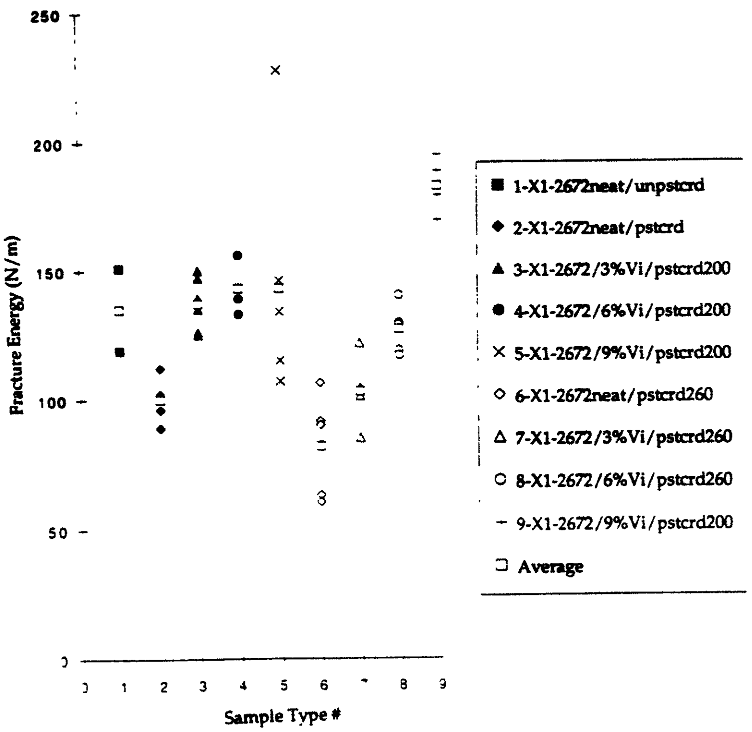


Figure 3.11: The fracture energy (G_{IC}) of X1-2672™ castings with vinyl terminated PDMS (DP_n=9), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

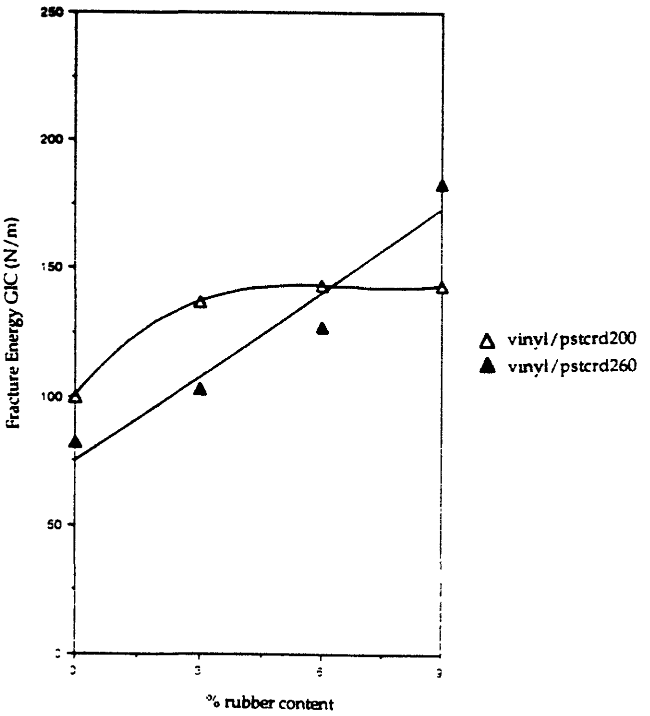


Figure 3.12: Variation of the average fracture energy (G_{IC}) with rubber content for X1-2672™ castings with vinyl terminated PDMS (DP_n=9), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

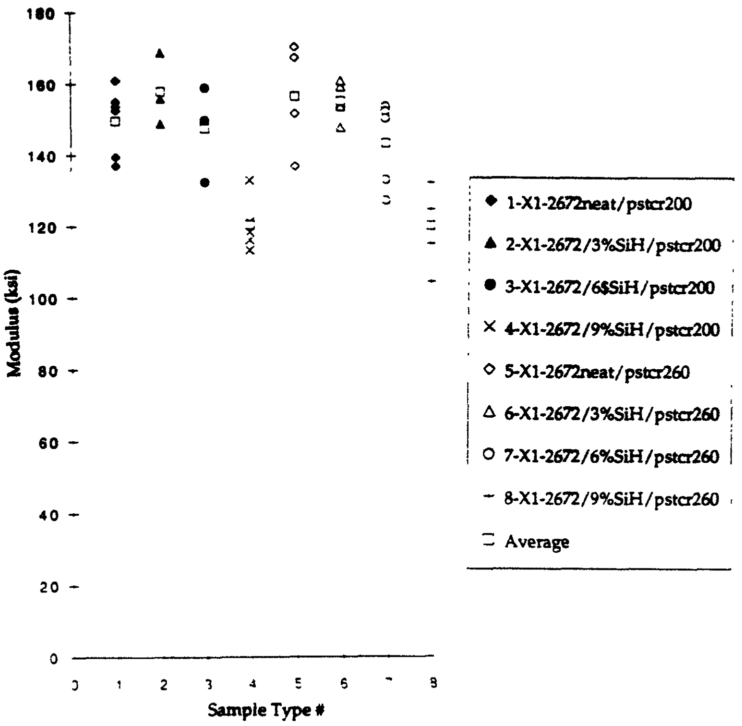


Figure 3.13: The flexural modulus of X1-2672™ castings with silane terminated rubber (DP_n=4), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

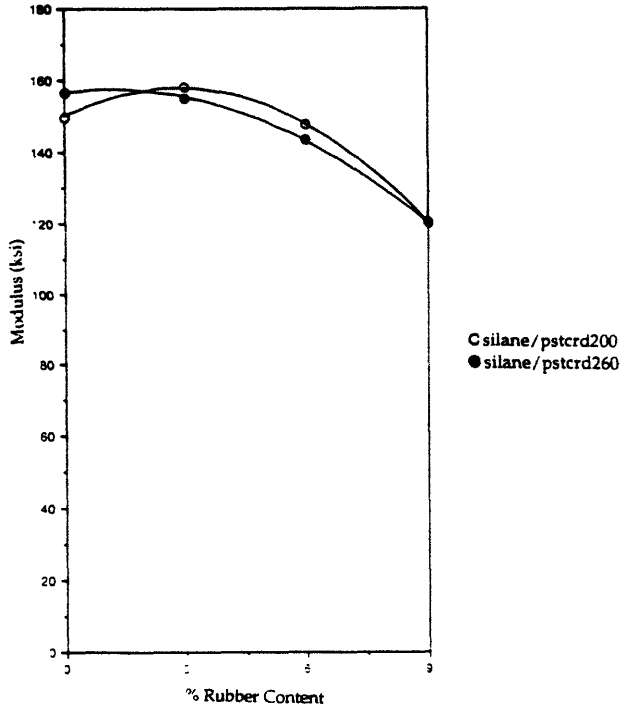


Figure 3.14: Variation of the average flexural modulus with rubber content for X1-2672 ™ castings with silane terminated rubber (DP_n=4), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

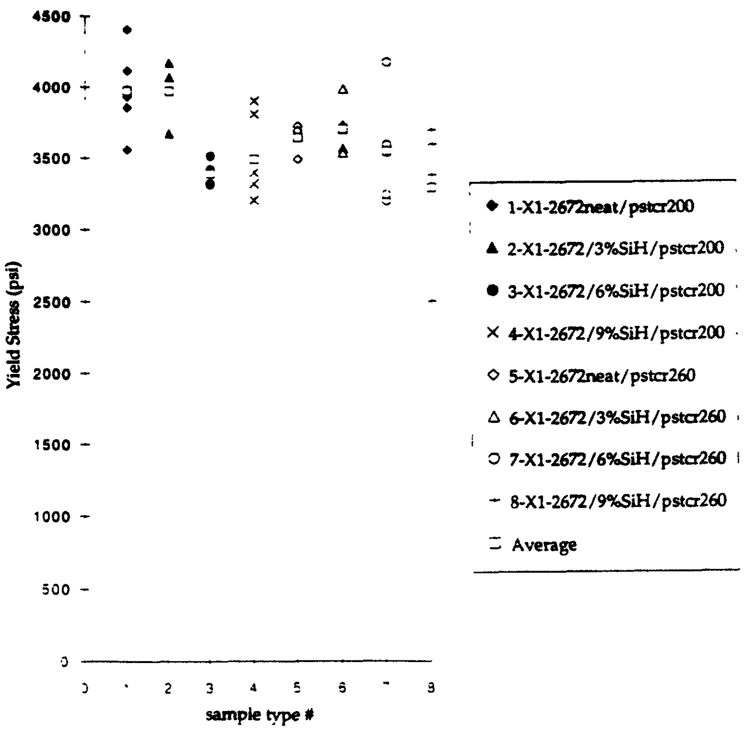


Figure 3.15: The flexural strength of X1-2672™ castings with silane terminated rubber (DP_n=4), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

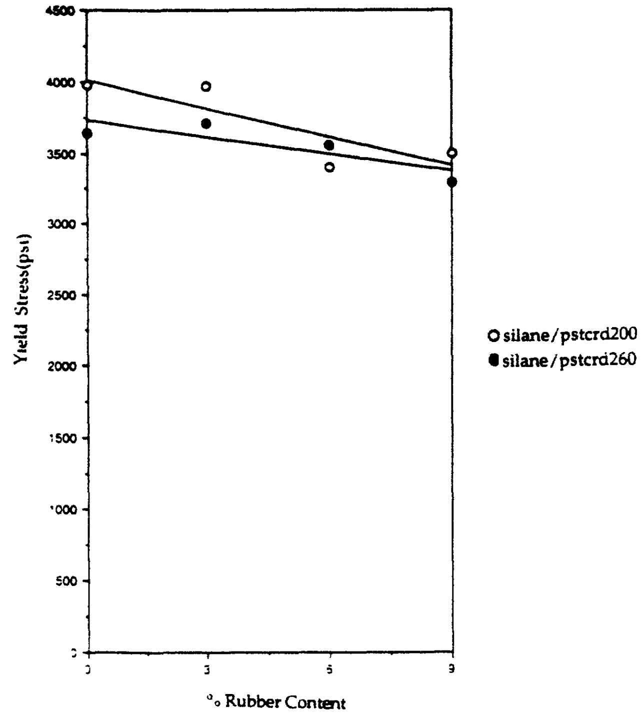


Figure 3.16: Variation of the average flexural strength with rubber content for X1-2672™ castings with silane terminated rubber (DP_n=4), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

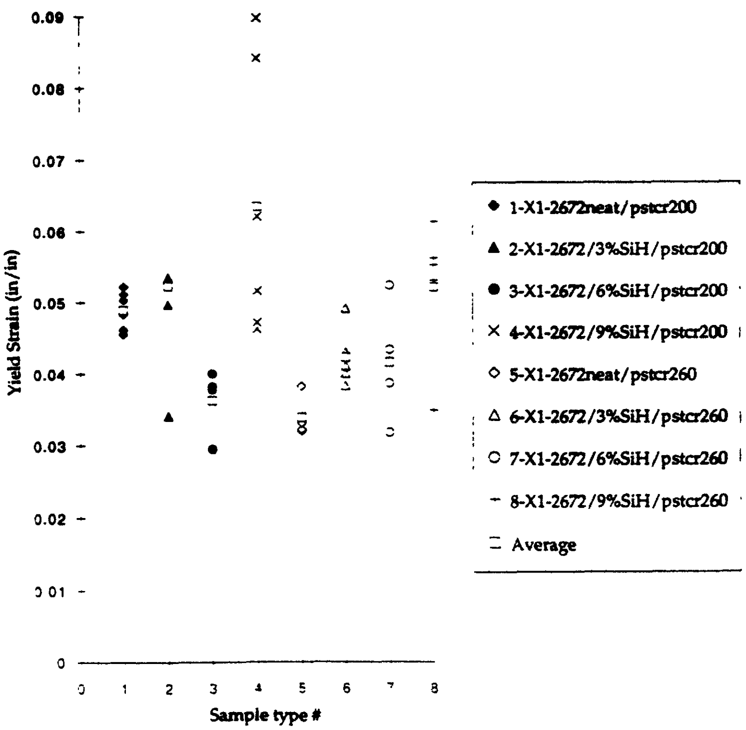


Figure 3.17: The yield strain of X1-2672™ castings with silane terminated rubber (DP_n=4), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

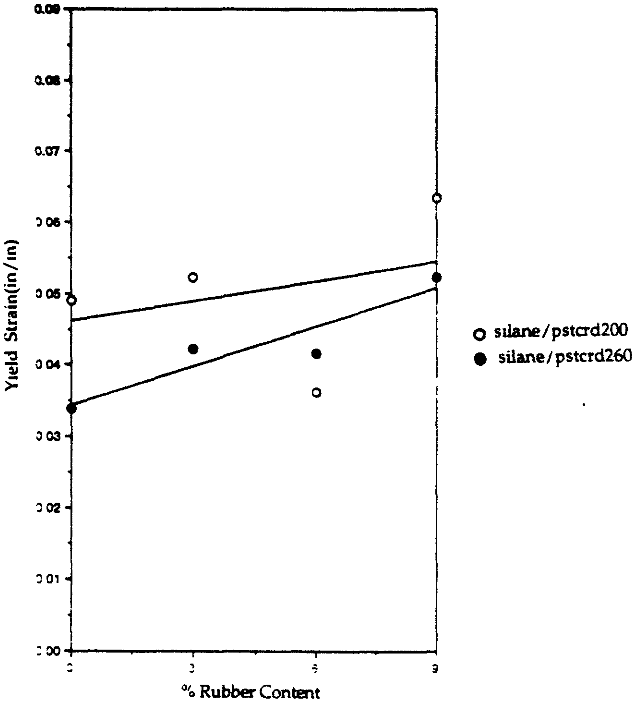


Figure 3.18: Variation of the average yield strain with rubber content for X1-2672™ castings with silane terminated rubber (DP_n=4), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

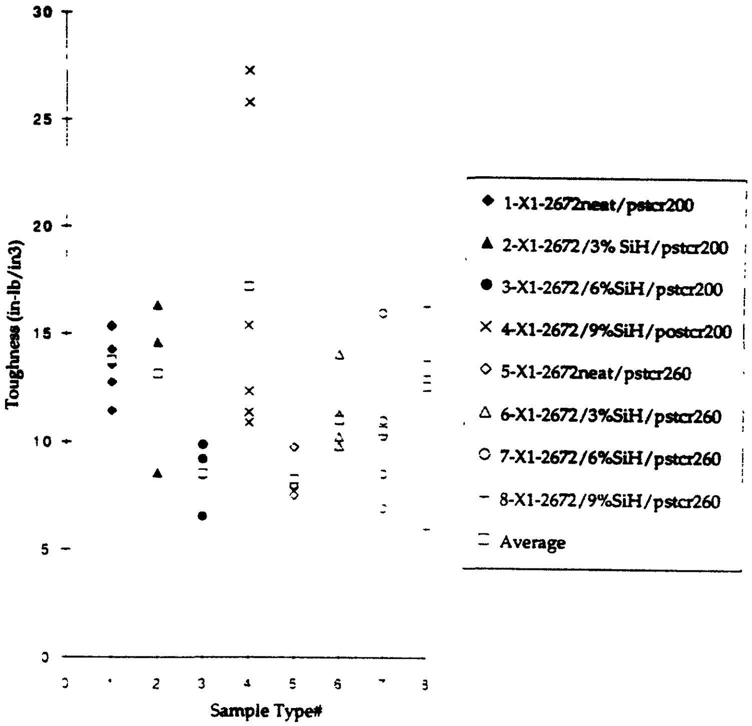


Figure 3.19: The toughness (load-displacement integral) of X1-2672™ castings with silane terminated rubber (DP_n=4), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

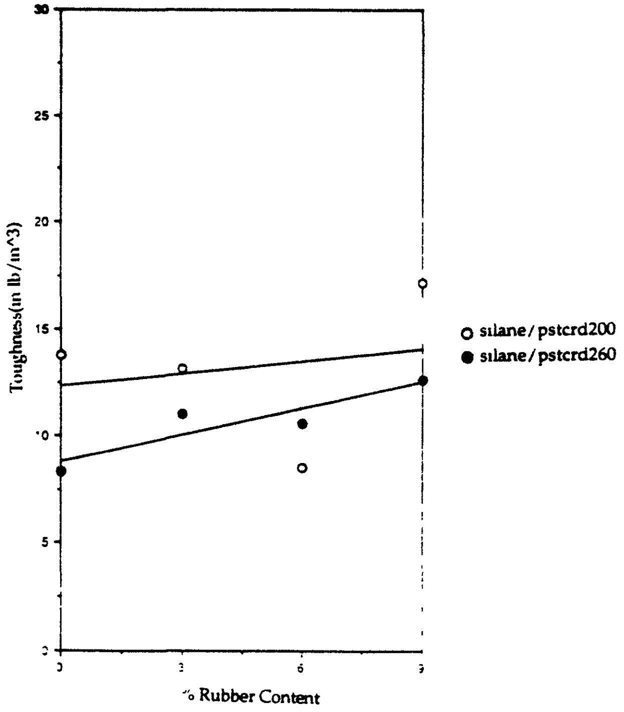


Figure 3.20: Variation of the average toughness (load-displacement integral) with rubber content for X1-2672™ castings with silane terminated rubber (DP_n=4), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

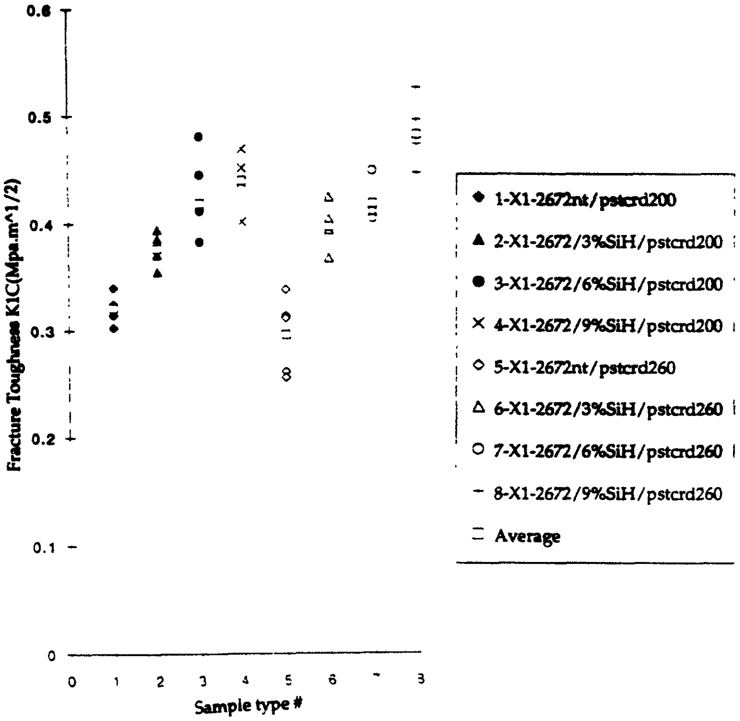


Figure 3.21: The fracture toughness (K_{IC}) of X1-2672™ castings with silane terminated rubber (DP_n=4), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

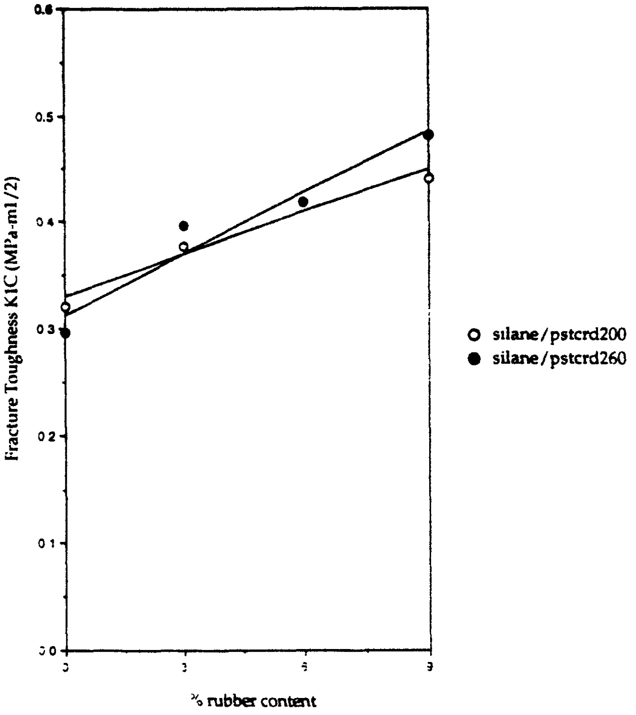


Figure 3.22: Variation of the average fracture toughness (K_{IC}) with rubber content for X1-2672™ castings with silane terminated rubber (DP_n=4), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

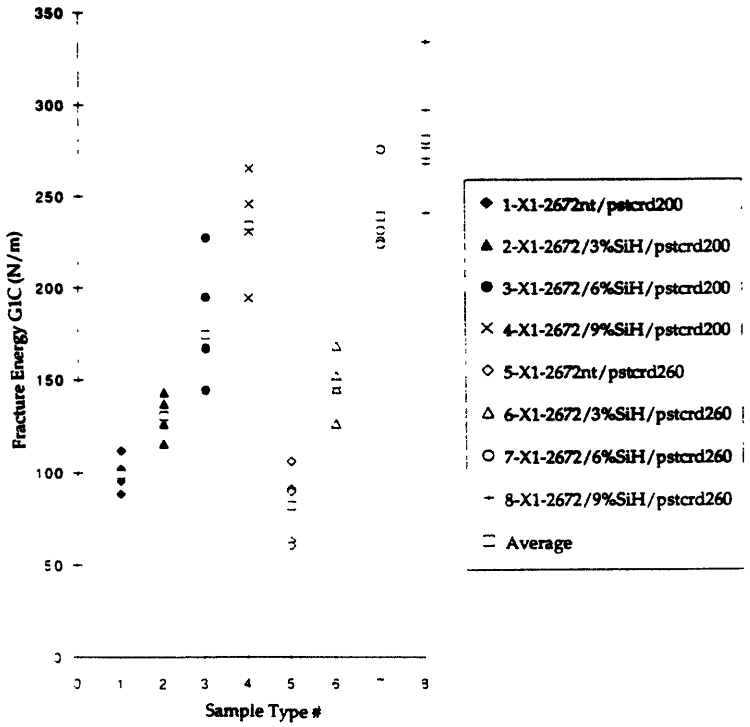


Figure 3.23: The fracture energy (G_{IC}) of X1-2672™ castings with silane terminated rubber (DP_n=4), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

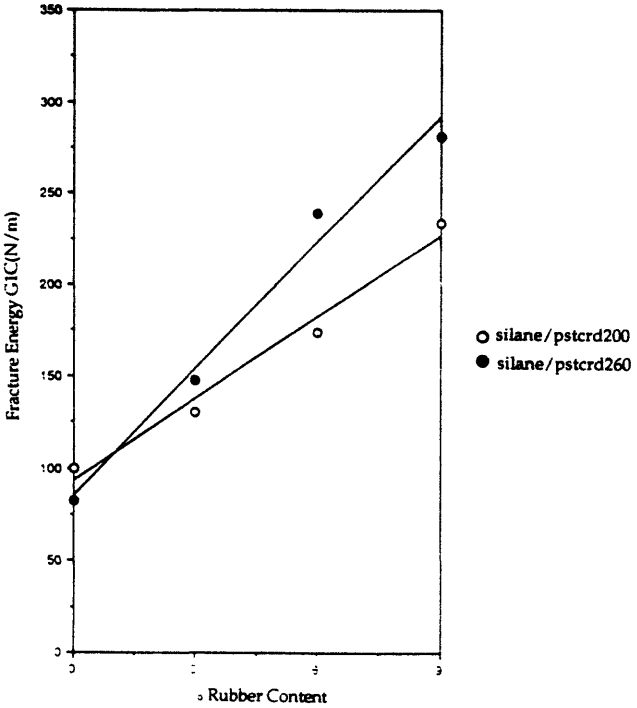


Figure 3.24: Variation of the average fracture energy (G_{IC}) with rubber content for X1-2672™ castings with silane terminated rubber (DP_n=4), post-cured at 200°C/4 hours and 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

3.1.2 Effect of rubber content on the flexural and fracture properties X1-2672™ with vinyl and silane terminated rubber.

Three-point bend and fracture toughness testing of X1-2672™ with 0,3,6,9, 12 and 15% vinyl terminated PDMS and 0,3,6,9, 12 and 15% silane terminated rubber, cured at 160°C for 16 hours and post-cured at 260°C for 8 hours with the trifunctional cross-linker, are shown in Figures 3.25-3.48. The flexural and fracture toughness testing data are available in Appendices B-1 to B-12 .

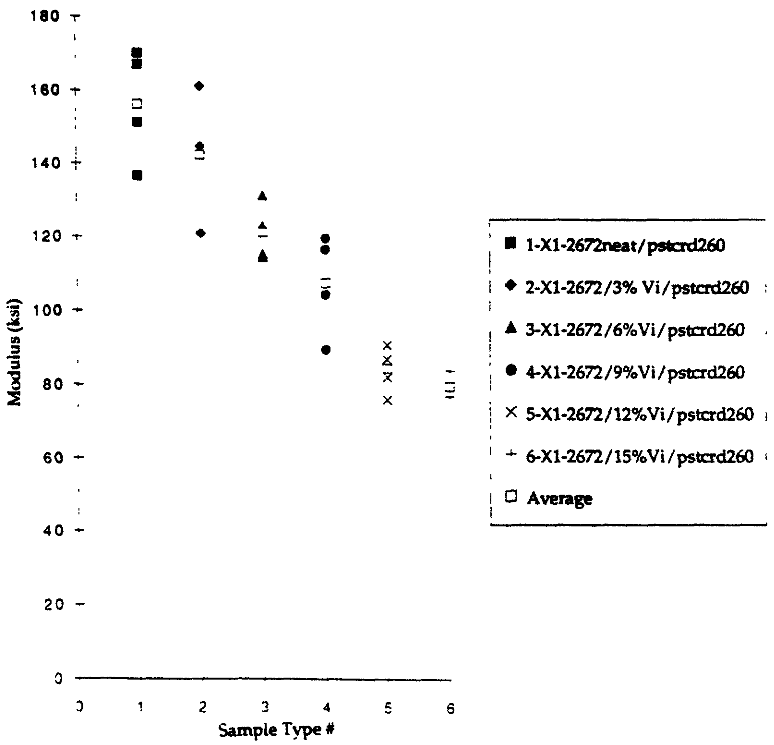


Figure 3.25: The flexural modulus of X1-2672™ castings with 0-15% vinyl terminated PDMS (DP_n=9), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

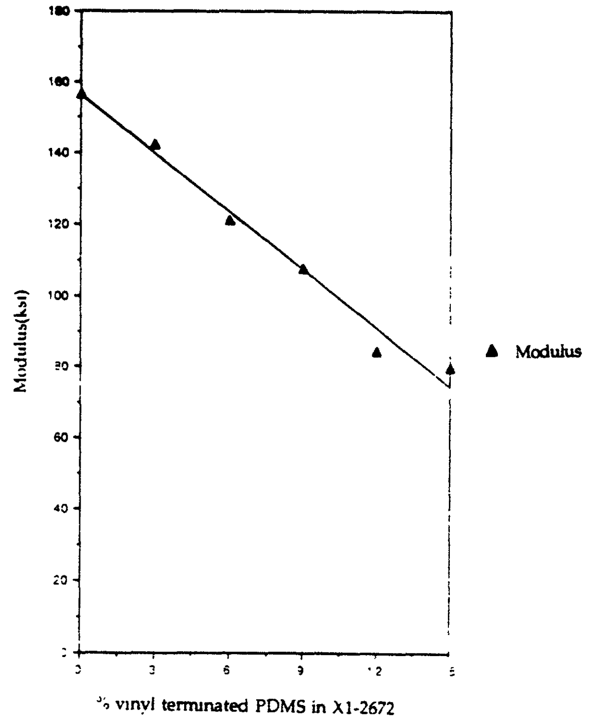


Figure 3.26: Variation of the average flexural modulus with rubber content for X1-2672™ castings with 0-15% vinyl terminated PDMS (DP_n=9), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

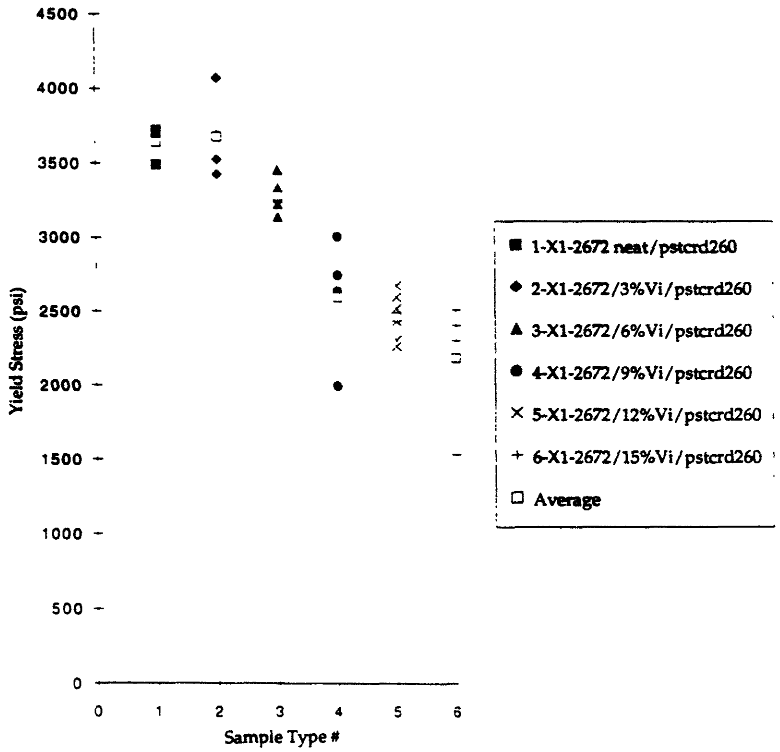


Figure 3.27: The flexural strength of X1-2672™ castings with 0-15% vinyl terminated PDMS (DP_n=9), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

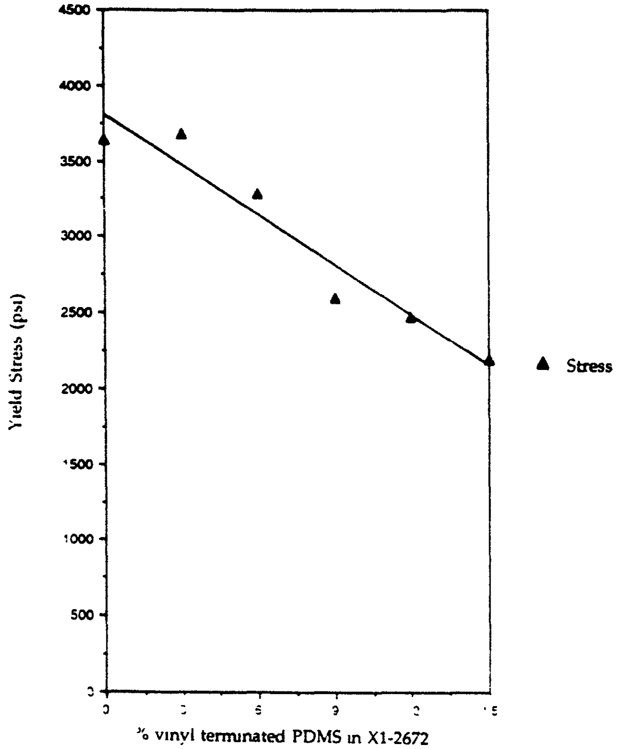


Figure 3.28: Variation of the average flexural strength with rubber content for X1-2672™ castings with 0-15% vinyl terminated PDMS (DP_n=9), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

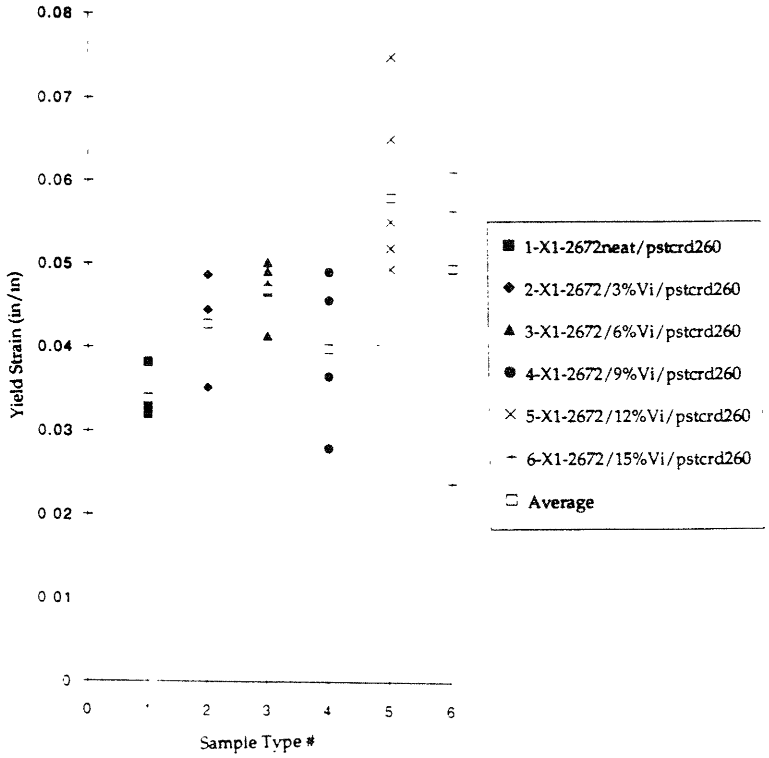


Figure 3.29: The yield strain of X1-2672™ castings with 0-15% vinyl terminated PDMS ($DP_n=9$), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

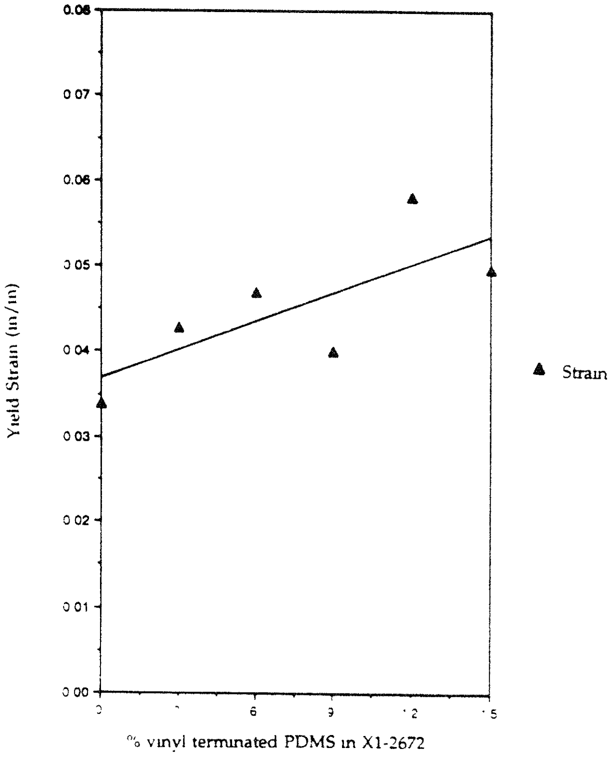


Figure 3.30: Variation of the average yield strain with rubber content for X1-2672™ castings with 0-15% vinyl terminated PDMS ($DP_n=9$), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

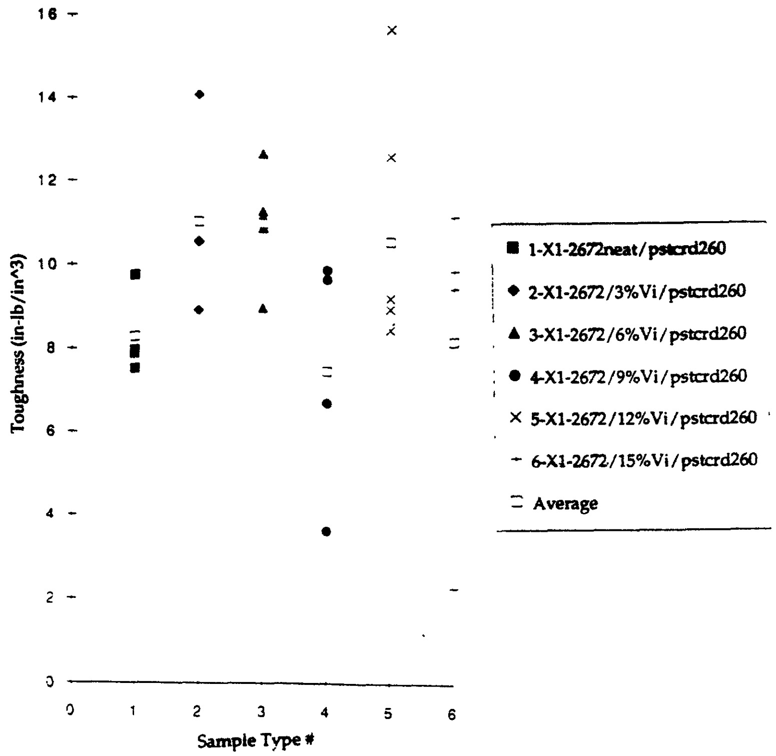


Figure 3.31: The toughness (load-displacement integral) of X1-2672™ castings with 0-15% vinyl terminated PDMS (DP_n=9), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

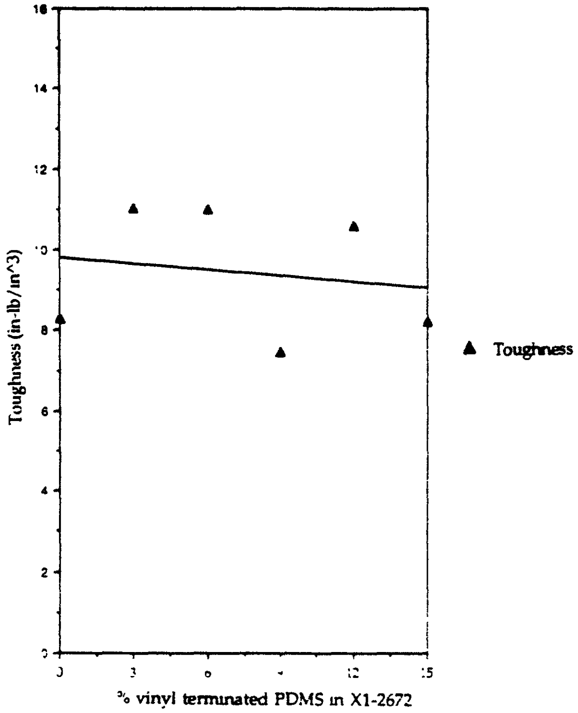


Figure 3.32: Variation of the average toughness (load-displacement integral) with rubber content for X1-2672™ castings with 0-15% vinyl terminated PDMS (DP_n=9), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

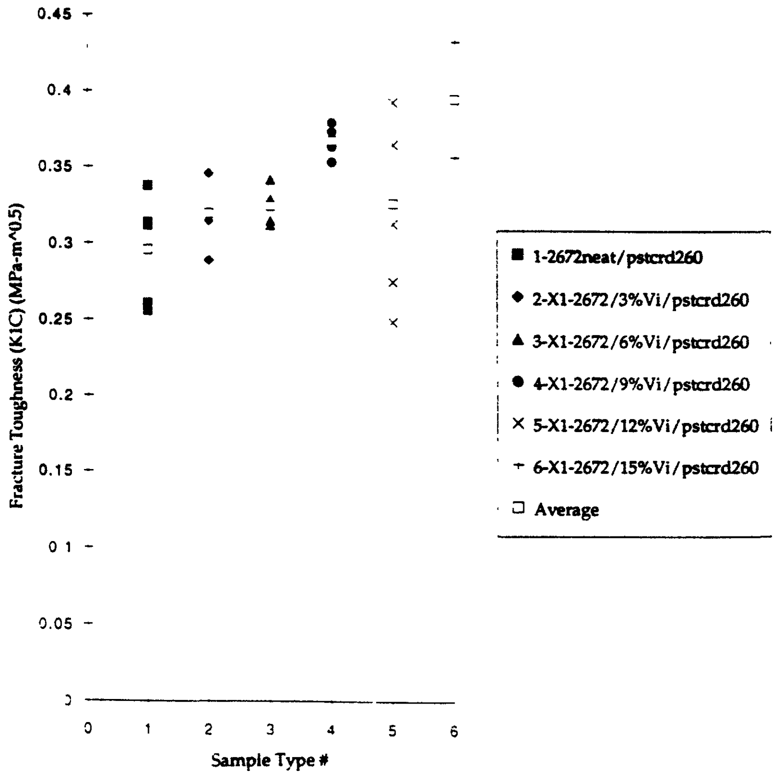


Figure 3.33: The fracture toughness (K_{IC}) of X1-2672™ castings with 0-15% vinyl terminated PDMS (DP_n=9), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

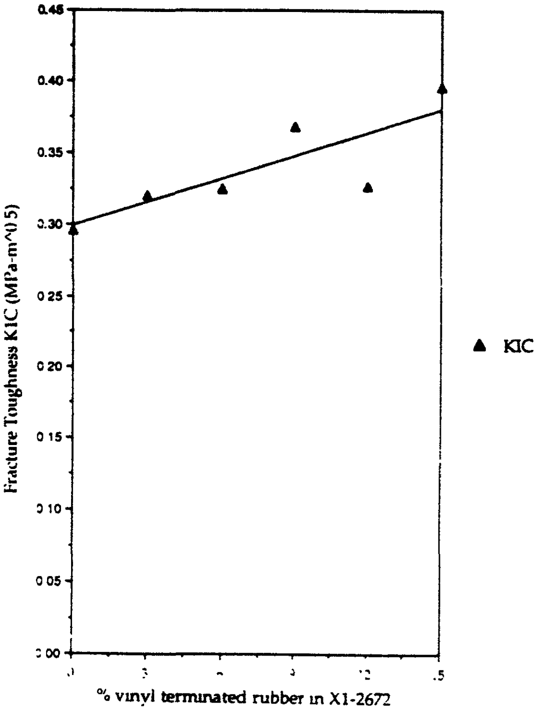


Figure 3.34: Variation of the average fracture toughness (K_{IC}) with rubber content for X1-2672™ castings with 0-15% vinyl terminated PDMS (DP_n=9), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

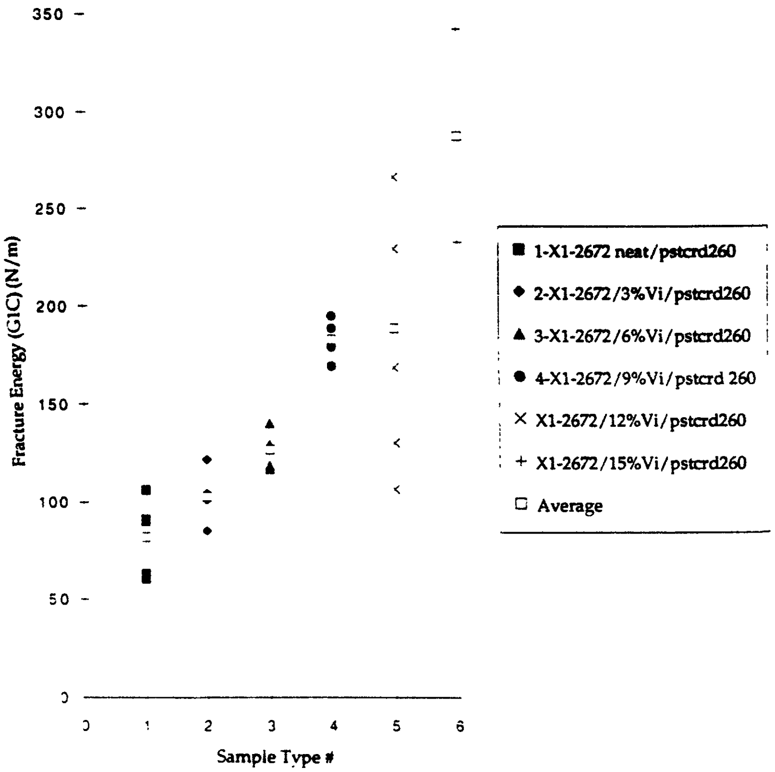


Figure 3.35: The fracture energy (G_{IC}) of X1-2672™ castings with 0-15% vinyl terminated PDMS (DP_n=9), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

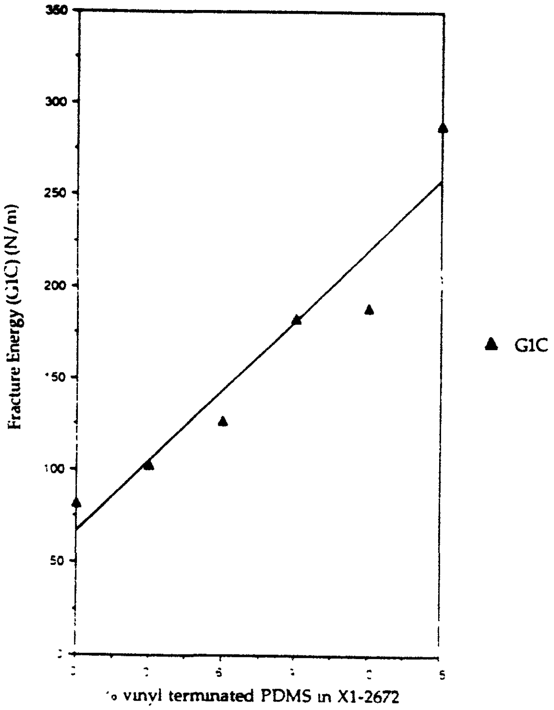


Figure 3.36: Variation of the average fracture energy (G_{IC}) with rubber content for X1-2672™ castings with 0-15% vinyl terminated PDMS (DP_n=9), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

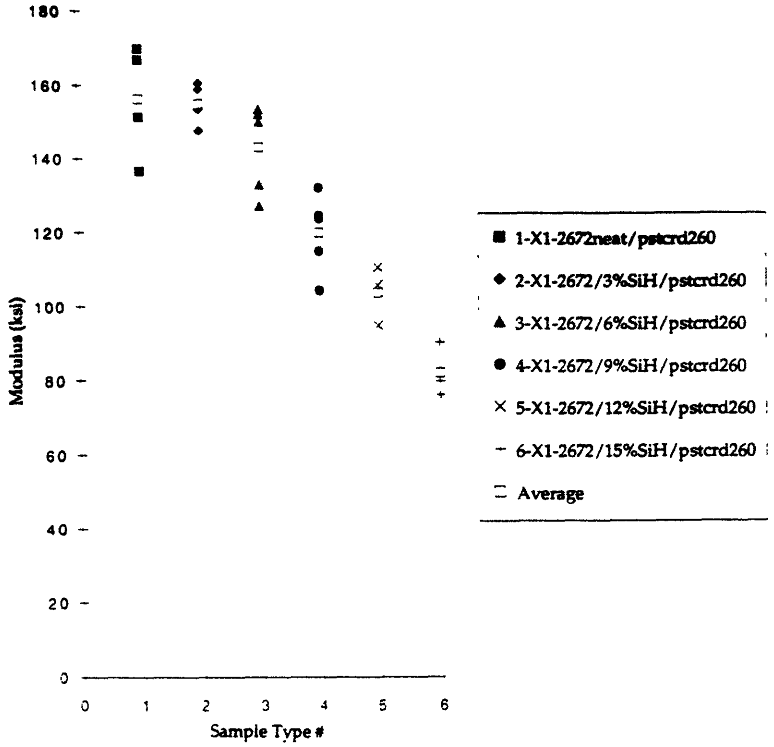


Figure 3.37: The flexural modulus of X1-2672™ castings with 0-15% silane terminated rubber (DP_n=4), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

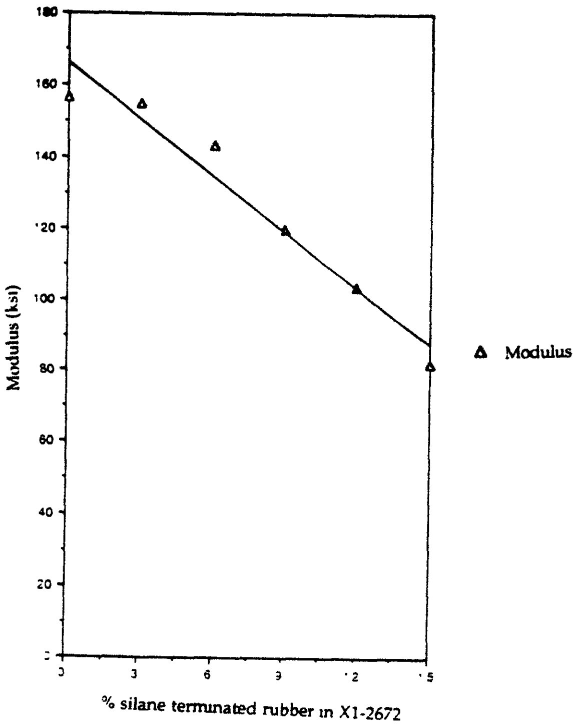


Figure 3.38: Variation of the average flexural modulus with rubber content for X1-2672™ castings with 0-15% silane terminated rubber (DP_n=4), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

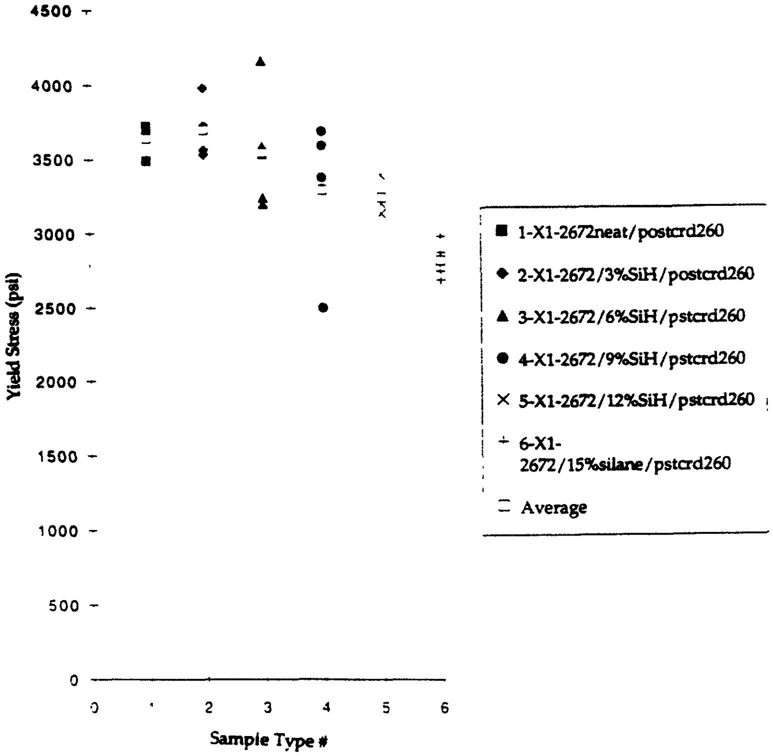


Figure 3.39: The flexural strength of X1-2672™ castings with 0-15% silane terminated rubber (DP_n=4), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

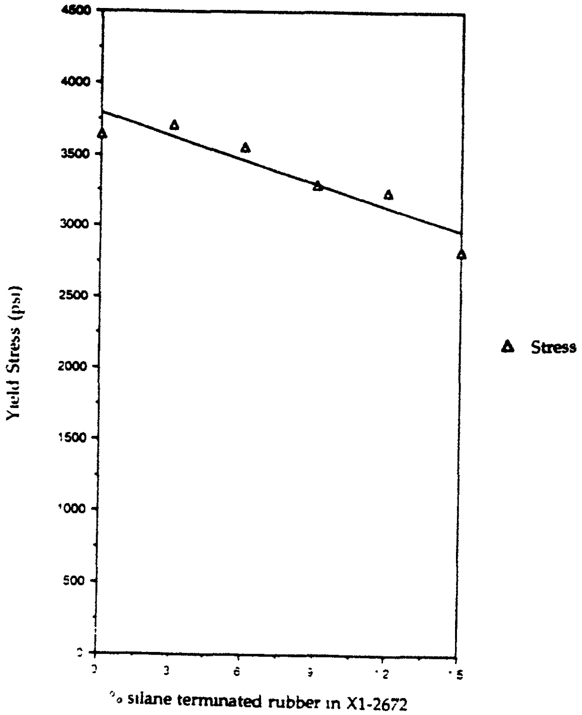


Figure 3.40: Variation of the average strength with rubber content for X1-2672™ castings with 0-15% silane terminated rubber (DP_n=4), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

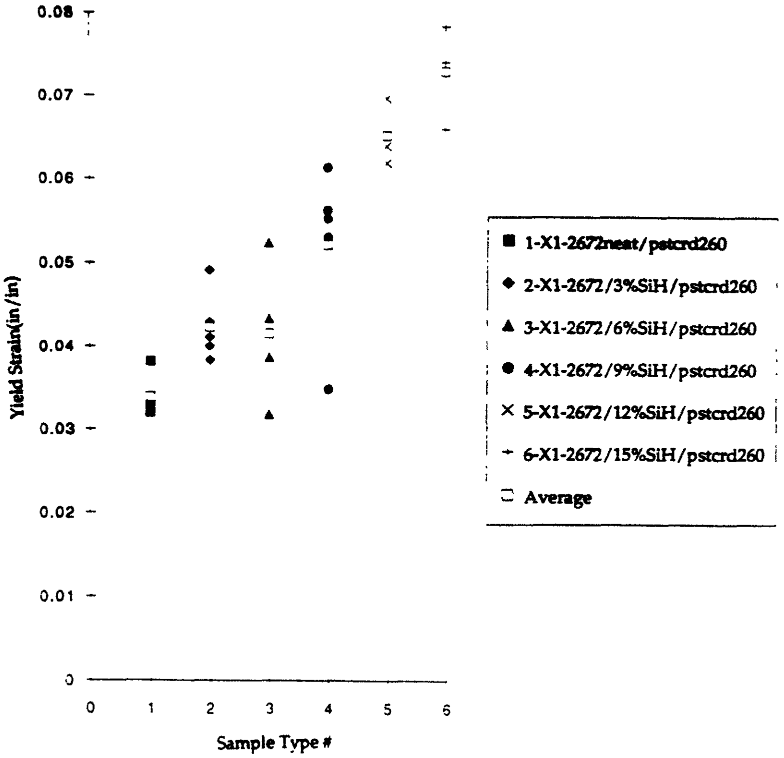


Figure 3.41: The yield strain of X1-2672™ castings with 0-15% silane terminated rubber (DP_n=4), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

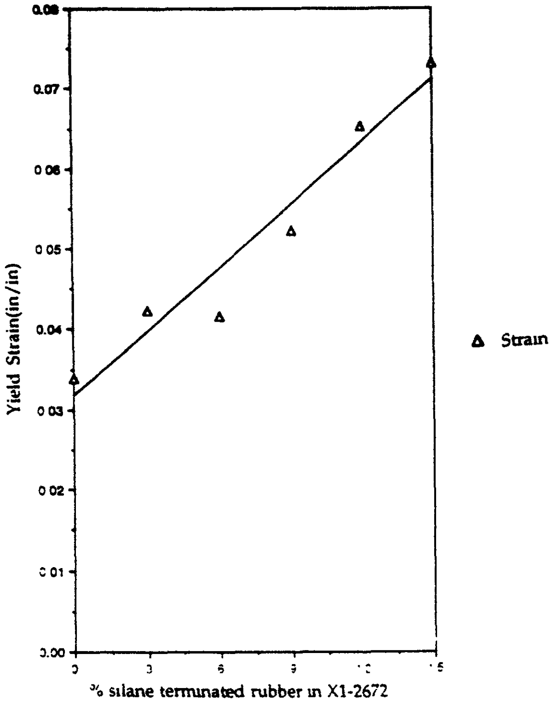


Figure 3.42: Variation of the average yield strain with rubber content for X1-2672™ castings with 0-15% silane terminated rubber (DP_n=4), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

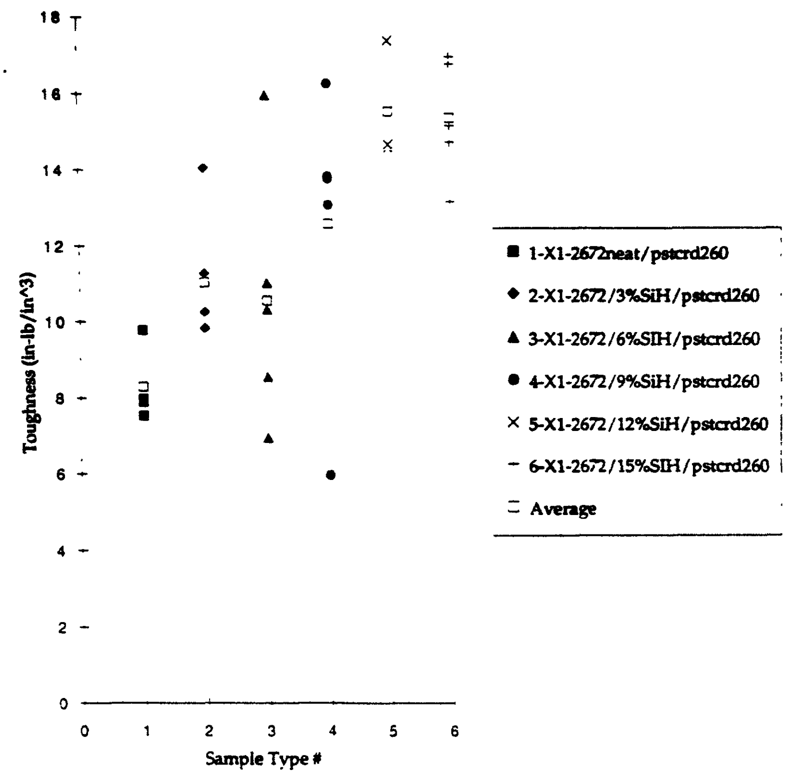


Figure 3.43: The toughness (load-displacement integral) of X1-2672™ castings with 0-15% silane terminated rubber (DP_n=4), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

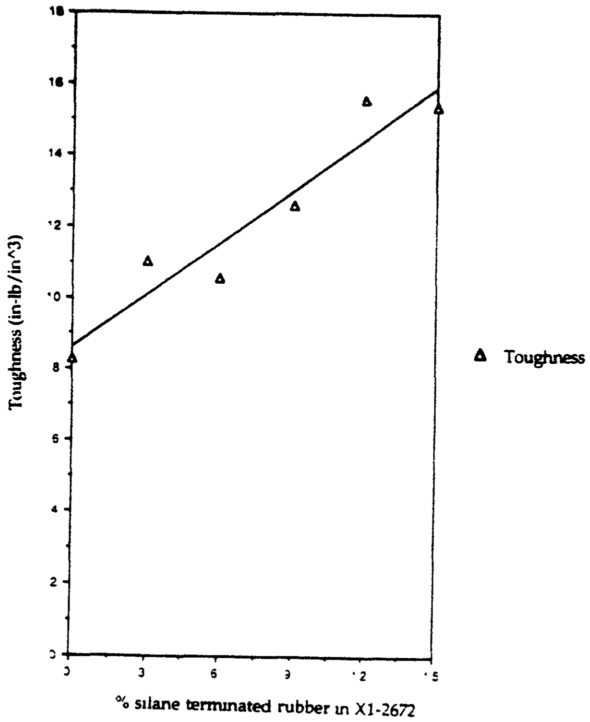


Figure 3.44: Variation of the average toughness (load-displacement integral) with rubber content for X1-2672™ castings with 0-15% silane terminated rubber (DP_n=4), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

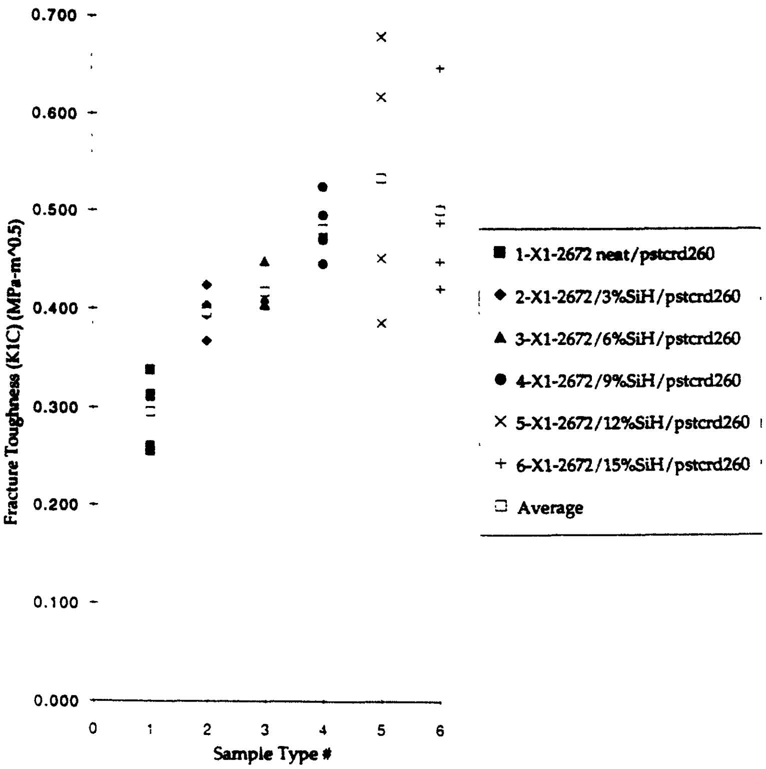


Figure 3.45: The fracture toughness (K_{IC}) of X1-2672™ castings with 0-15% silane terminated rubber (DP_n=4), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

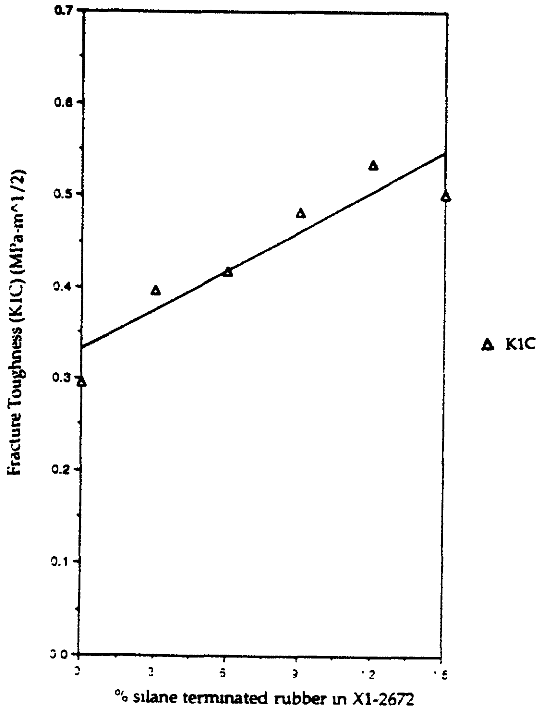


Figure 3.46: Variation of the average fracture toughness (K_{IC}) with rubber content for X1-2672™ castings with 0-15% silane terminated rubber (DP_n=4), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

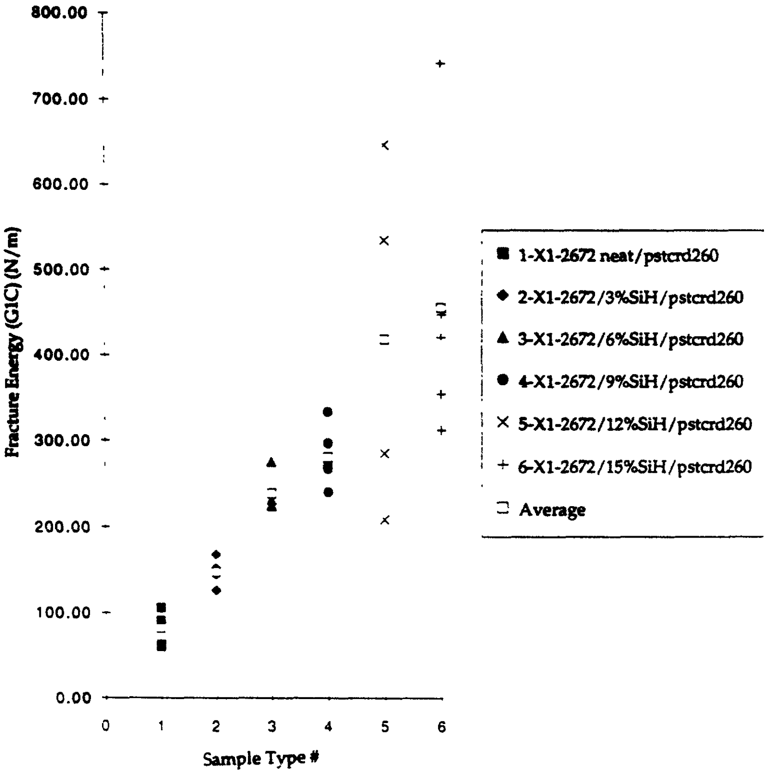


Figure 3.47: The fracture energy (G_{IC}) of X1-2672™ castings with 0-15% silane terminated rubber (DP_n=4), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

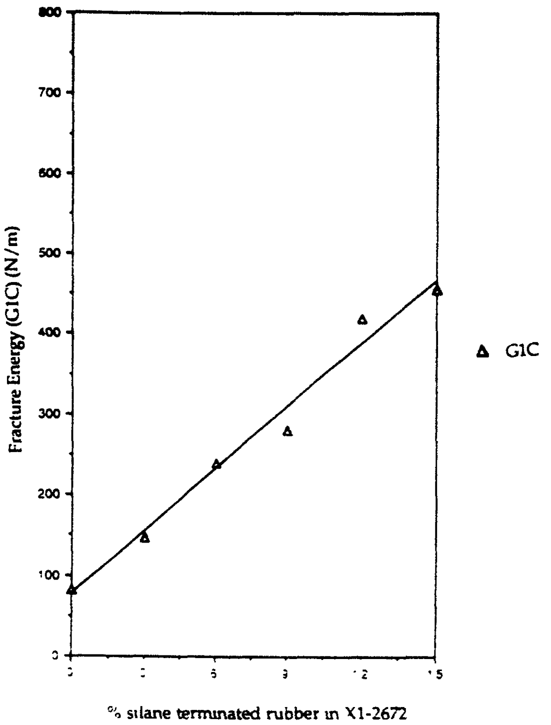


Figure 3.48: Variation of the average fracture energy (G_{IC}) with rubber content for X1-2672™ castings with 0-15% silane terminated rubber (DP_n=4), post-cured at 260°C/8 hours. All samples were cured with the trifunctional cross-linker.

3.1.3 Effect of cross-linker functionality on the flexural and fracture toughness properties of X1-2672™ with vinyl and silane terminated rubber.

The results of three-point bend tests of X1-2672™ with 0,3,6 and 9% vinyl terminated PDMS and 0,3,6 and 9% silane terminated rubber, cured at 160°C for 16 hours with the trifunctional cross-linker and cured at 140°C for 16 hours with the tetrafunctional cross-linker; both post-cured at 260°C for 8 hours are shown in Figures 3.49-3.72. The flexural and fracture toughness testing data are found in Appendices B-1 to B-12.

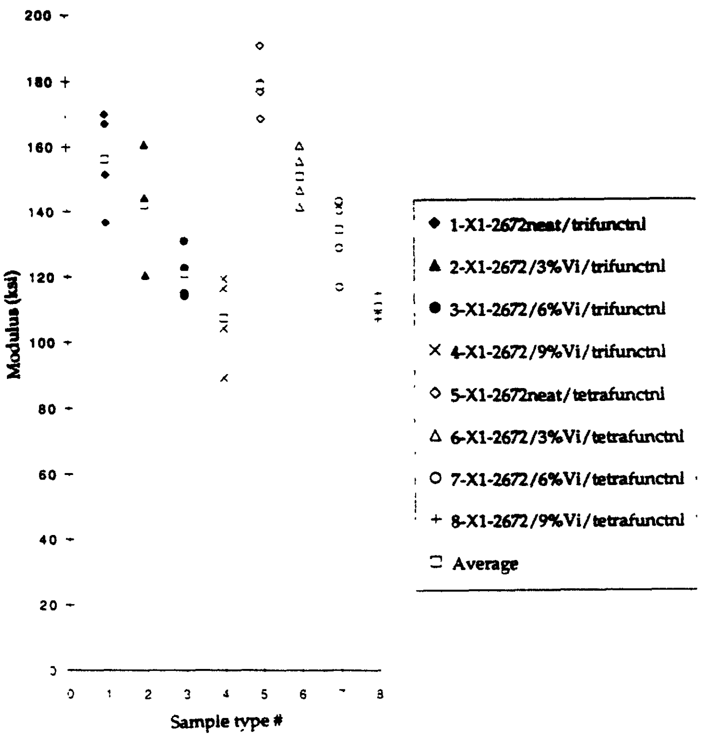


Figure 3.49: The flexural modulus of X1-2672™ castings with 0-9% vinyl terminated PDMS (DP_n=9), cured with tri and tetrafunctional cross-linkers. and post-cured at 260°C/8 hours.

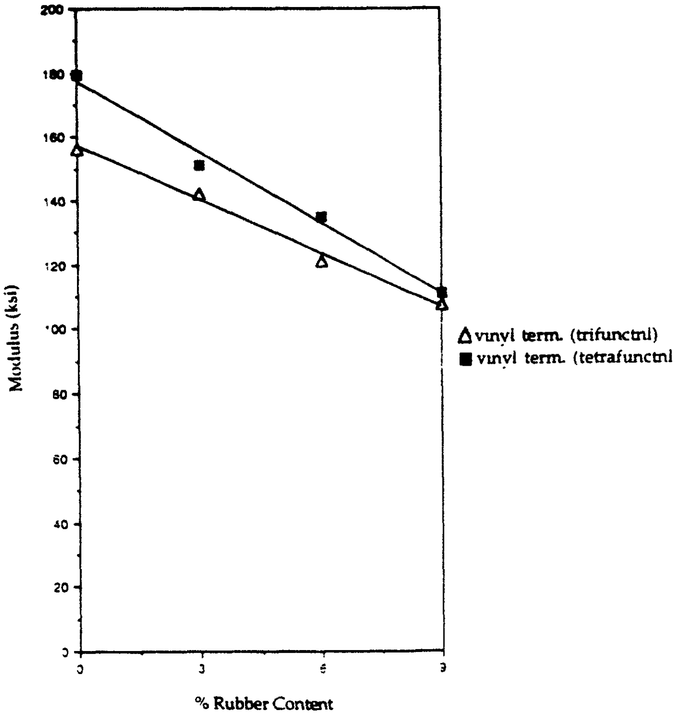


Figure 3.50: Variation of the average flexural modulus with rubber content for X1-2672™ castings with 0-9% vinyl terminated PDMS (DP_n=9), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours.

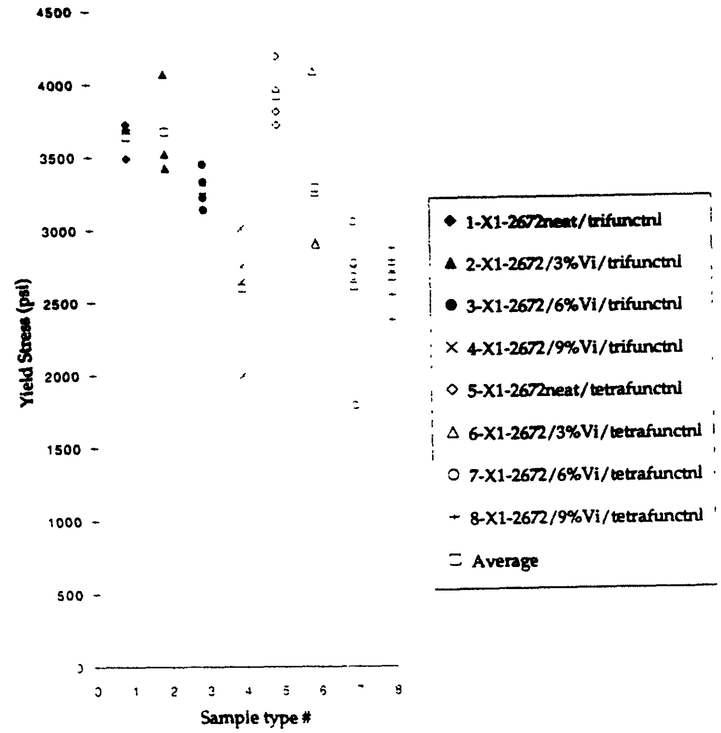


Figure 3.51: The flexural strength of X1-2672™ castings with 0-9% vinyl terminated PDMS (DP_n=9), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours.

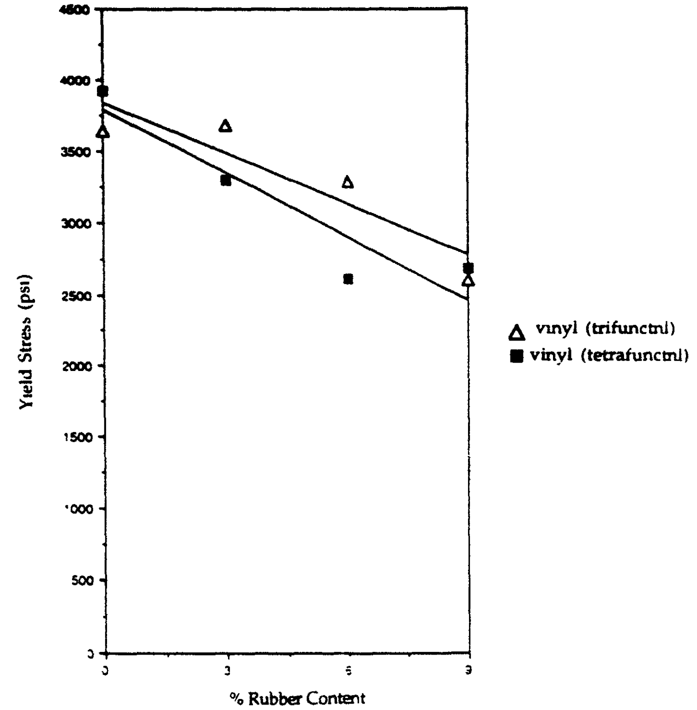


Figure 3.52: Variation of the average flexural strength with rubber content for X1-2672™ castings with 0-9% vinyl terminated PDMS (DP_n=9), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours.

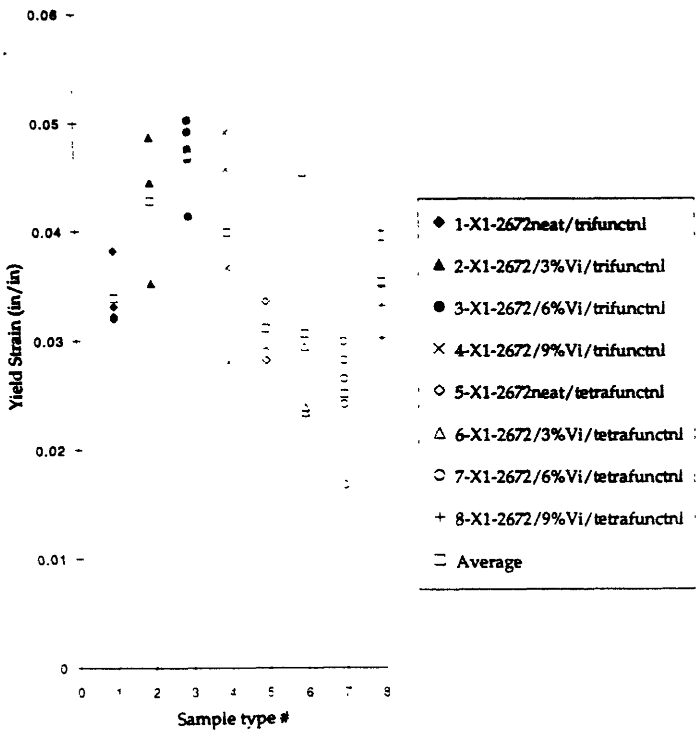


Figure 3.53: The yield strain of X1-2672™ castings with 0-9% vinyl terminated PDMS (DP_n=9), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours.

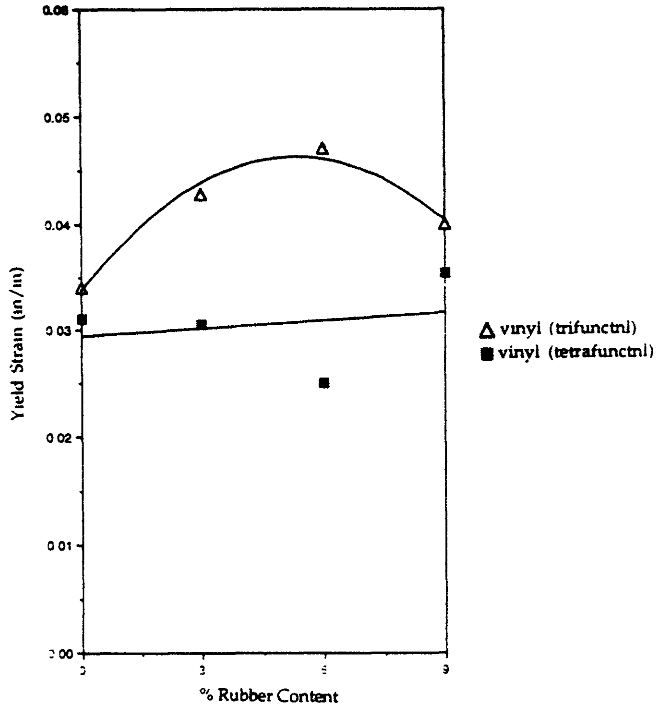


Figure 3.54: Variation of the average yield strain with rubber content for X1-2672™ castings with 0-9% vinyl terminated PDMS (DP_n=9), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours.

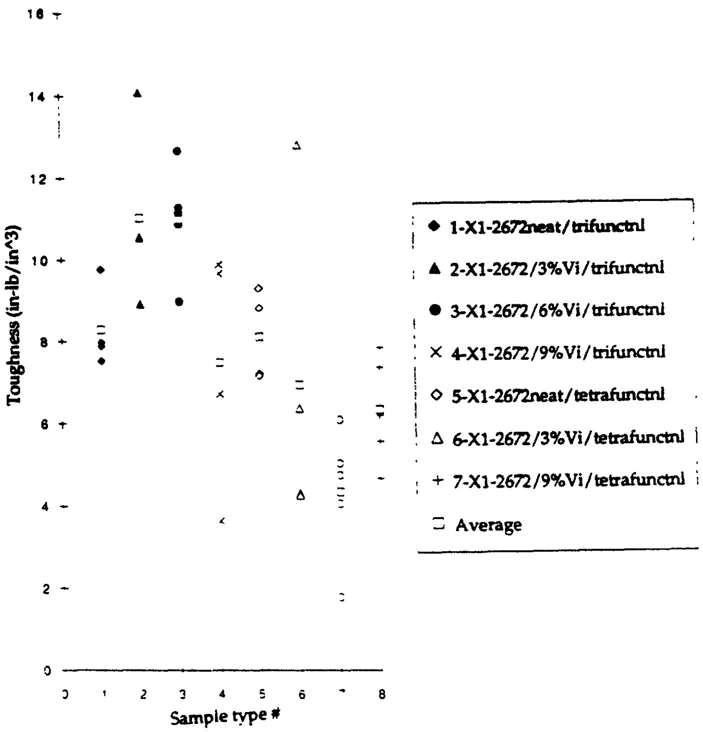


Figure 3.55 The toughness (load-displacement integral) of X1-2672™ castings with 0-9% vinyl terminated PDMS (DP_n=9), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours.

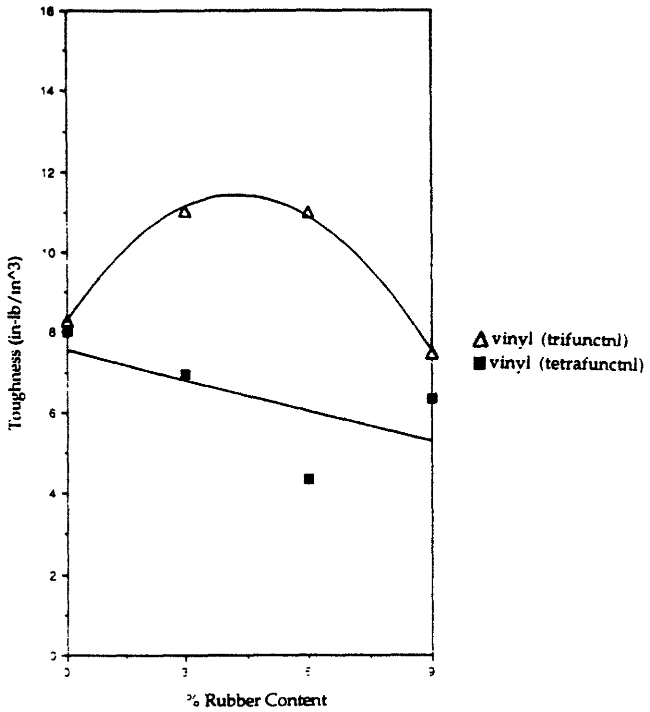


Figure 3.56: Variation of the average toughness (load-displacement integral) with rubber content for X1-2672™ castings with 0-9% vinyl terminated PDMS (DP_n=9), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours. .

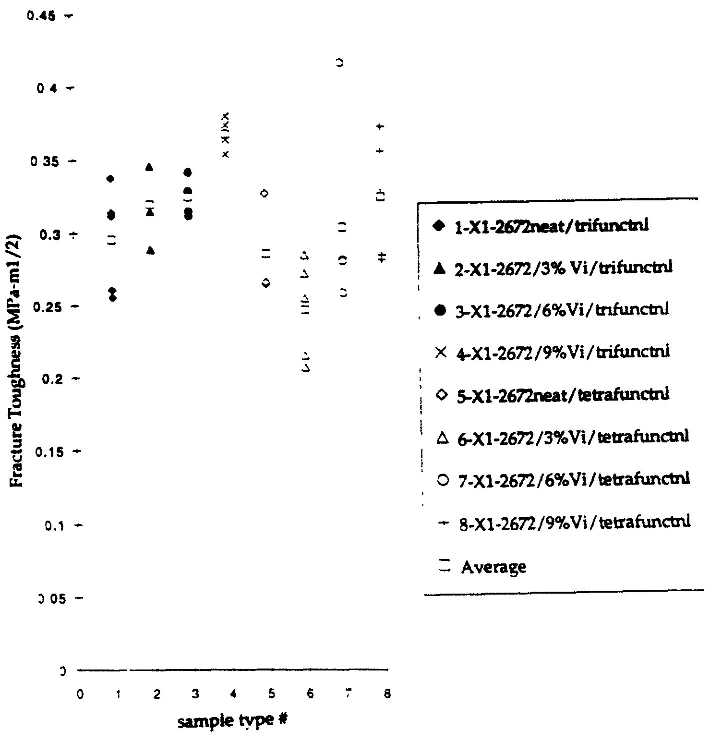


Figure 3.57: The fracture toughness (K_{IC}) of X1-2672™ castings with 0-9% vinyl terminated PDMS (DP_n=9), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours.

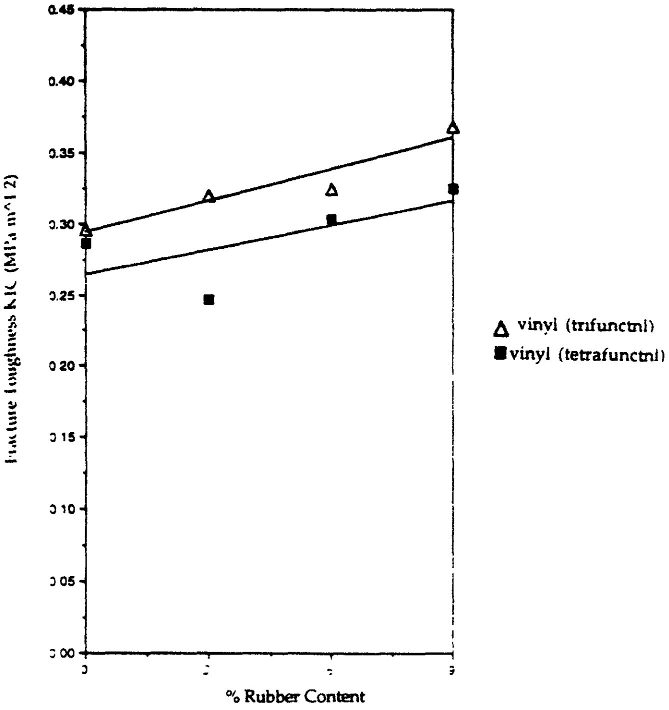


Figure 3.58: Variation of the average fracture toughness (K_{IC}) with rubber content for X1-2672™ castings with 0-9% vinyl terminated PDMS (DP_n=9), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours.

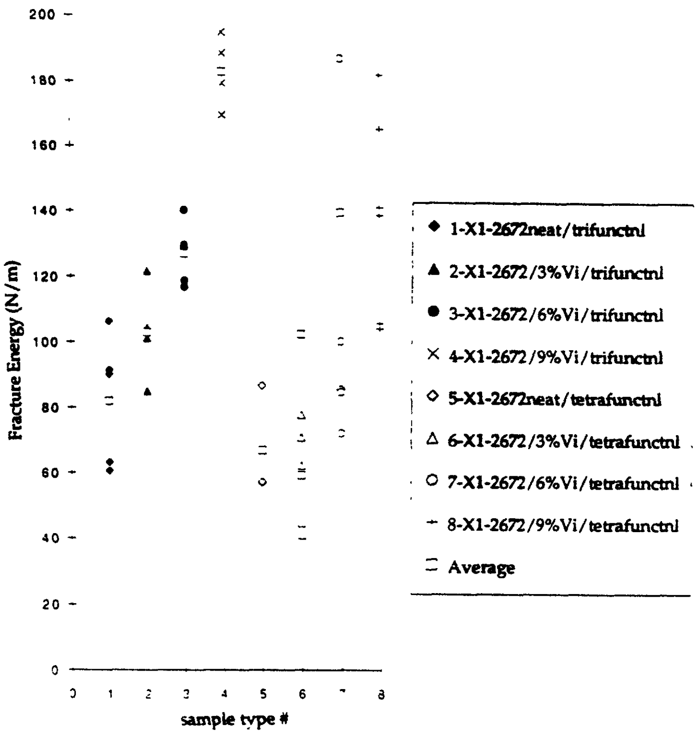


Figure 3.59: The fracture energy (G_{IC}) of X1-2672™ castings with 0-9% vinyl terminated PDMS (DP_n=9), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours.

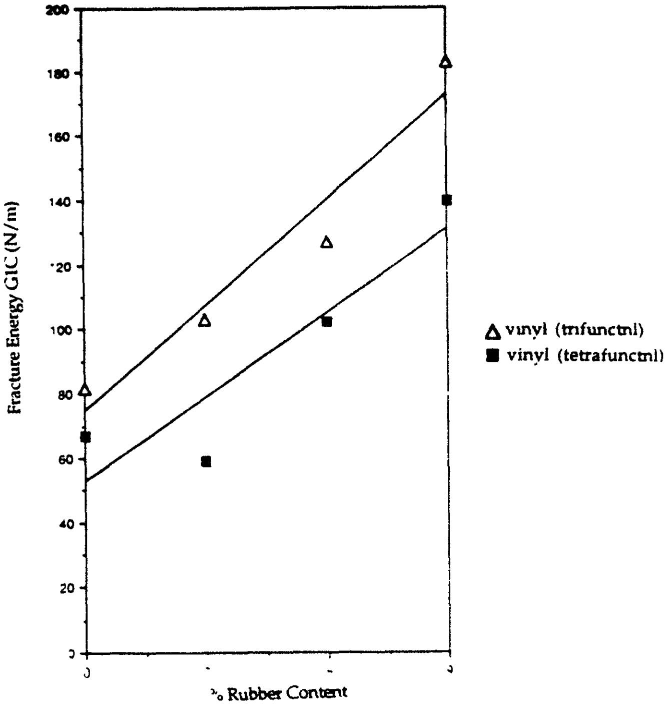


Figure 3.60: Variation of the average fracture energy (G_{IC}) with rubber content for X1-2672™ castings with 0-9% vinyl terminated PDMS (DP_n=9), cured with tri and tetrafunctional cross-linkers post-cured at 260°C/8 hours.

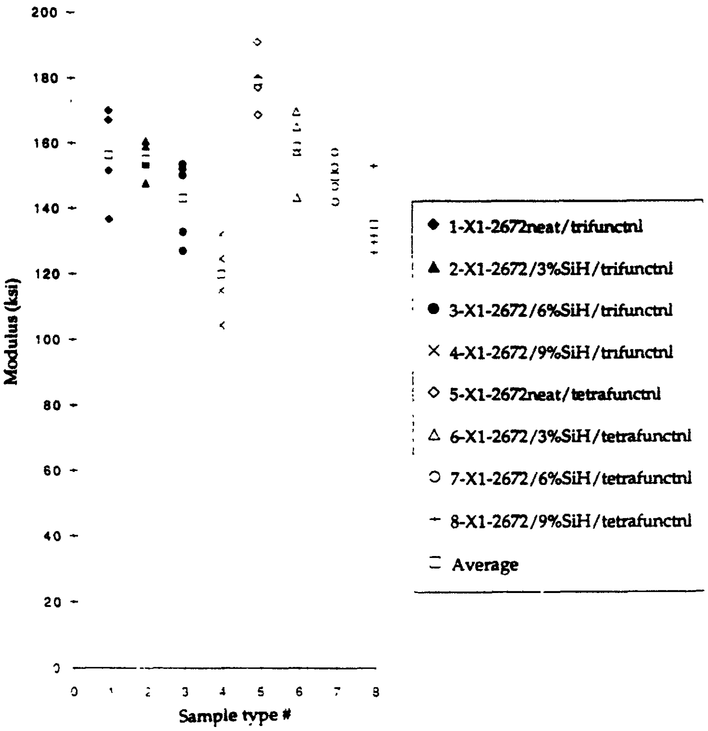


Figure 3.61: The flexural modulus of X1-2672™ castings with 0-9% silane terminated rubber (DP_n=4), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours.

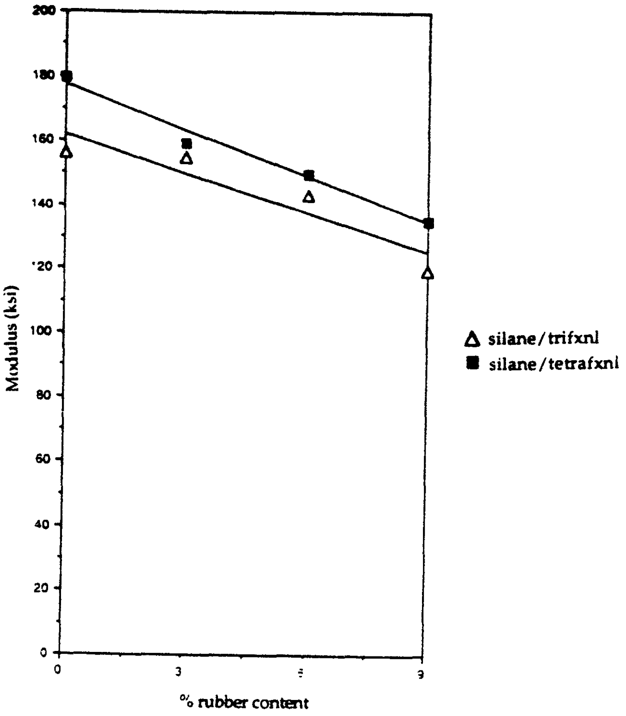


Figure 3.62: Variation of the average flexural modulus with rubber content for X1-2672™ castings with 0-9% silane terminated rubber (DP_n=4), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours.

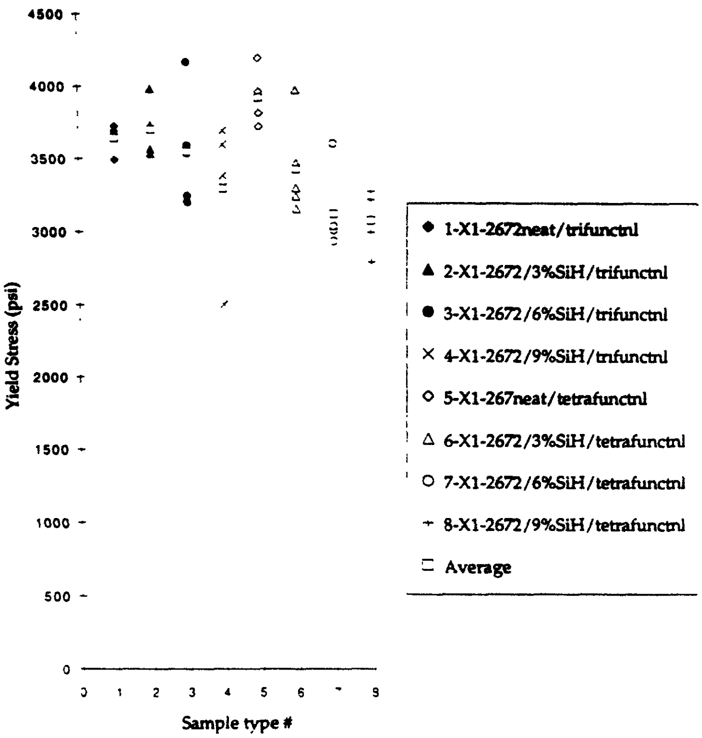


Figure 3.63: The flexural strength of X1-2672™ castings with 0-9% silane terminated rubber ($DP_n=4$), cured with tri and tetrafunctional cross-linkers and post-cured 260°C/8 hours.

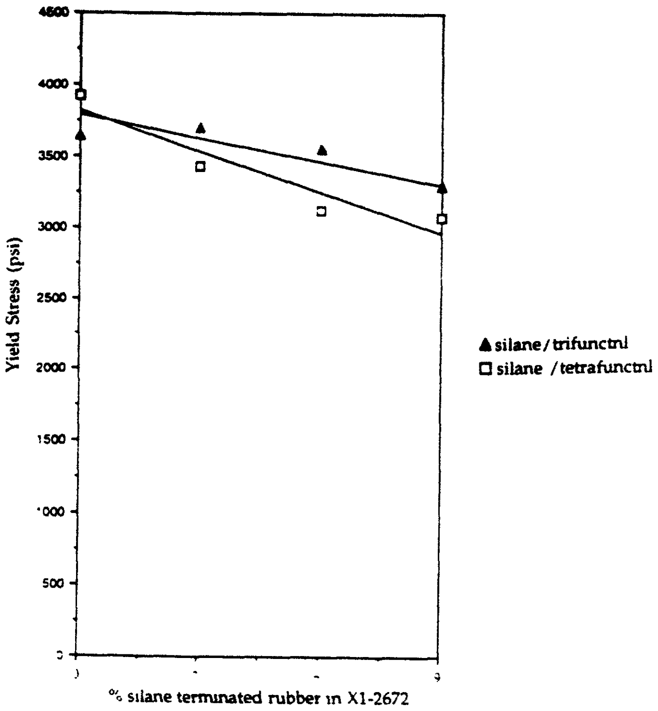


Figure 3.64: Variation of the average strength with rubber content for X1-2672™ castings with 0-9% silane terminated rubber ($DP_n=4$), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours.

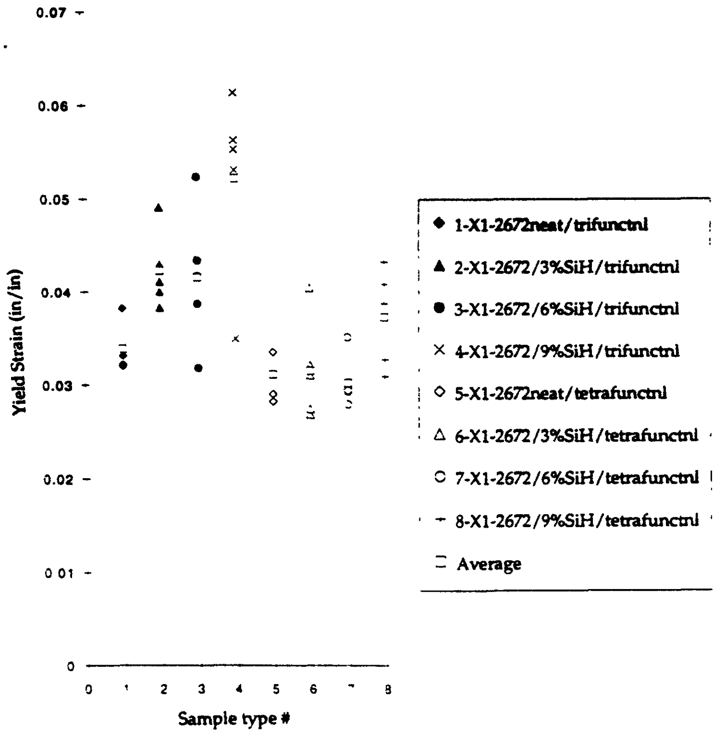


Figure 3.65: The yield strain of X1-2672™ castings with 0-9% silane terminated rubber (DP_n=4), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours.

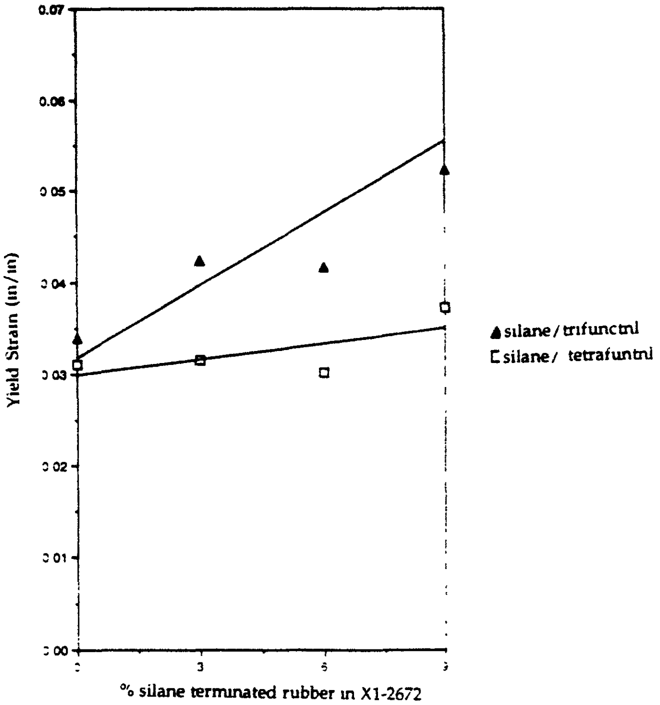


Figure 3.66: Variation of the average yield strain with rubber content for X1-2672™ castings with 0-9% silane terminated rubber (DP_n=4), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours.

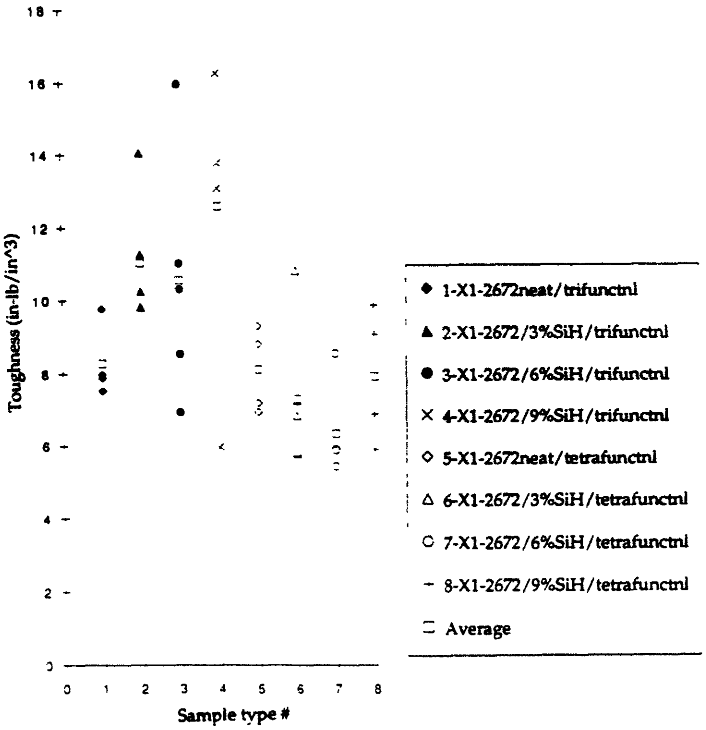


Figure 3.67: The toughness (load-displacement integral) of X1-2672™ castings with 0-9% silane terminated rubber (DP_n=4), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours.

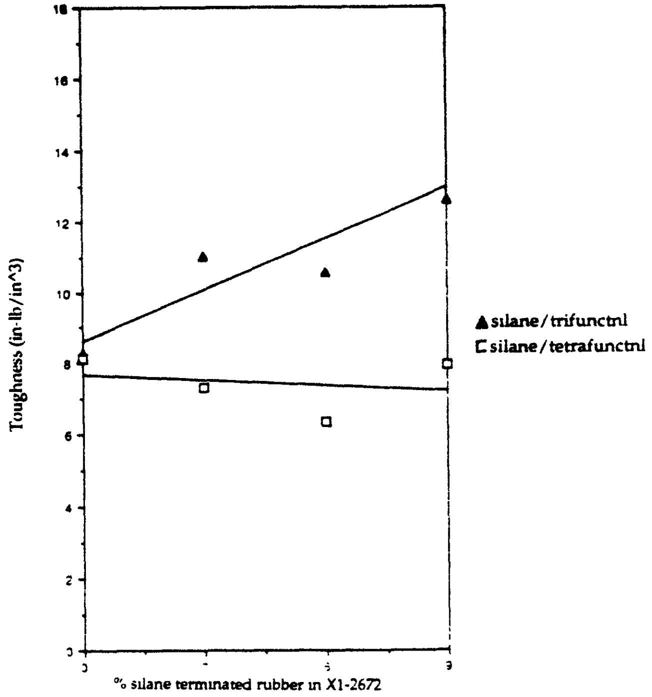


Figure 3.68: Variation of the average toughness (load-displacement integral) with rubber content for X1-2672™ castings with 0-9% silane terminated rubber (DP_n=4), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours.

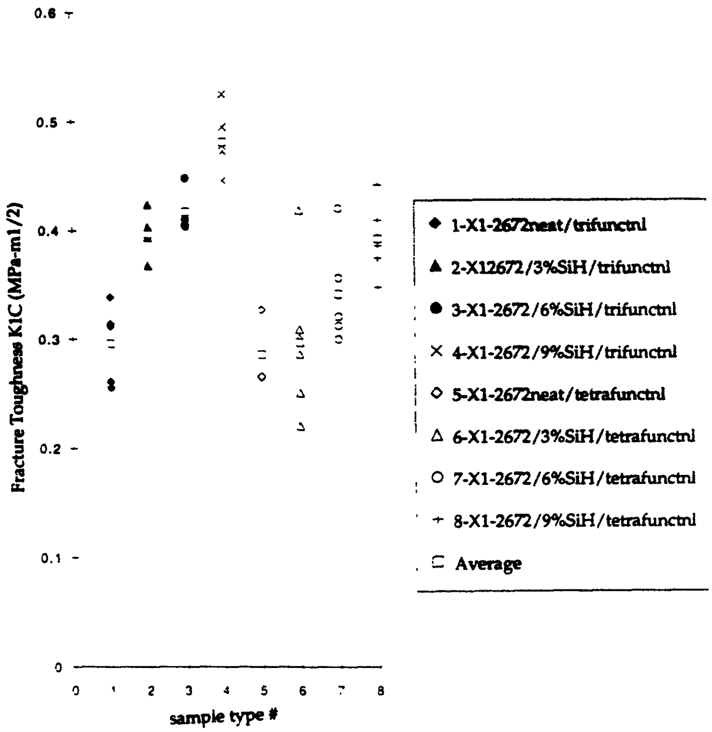


Figure 3.69: The fracture toughness (K_{IC}) of X1-2672™ castings with 0-9% silane terminated rubber (DP_n=4), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours.

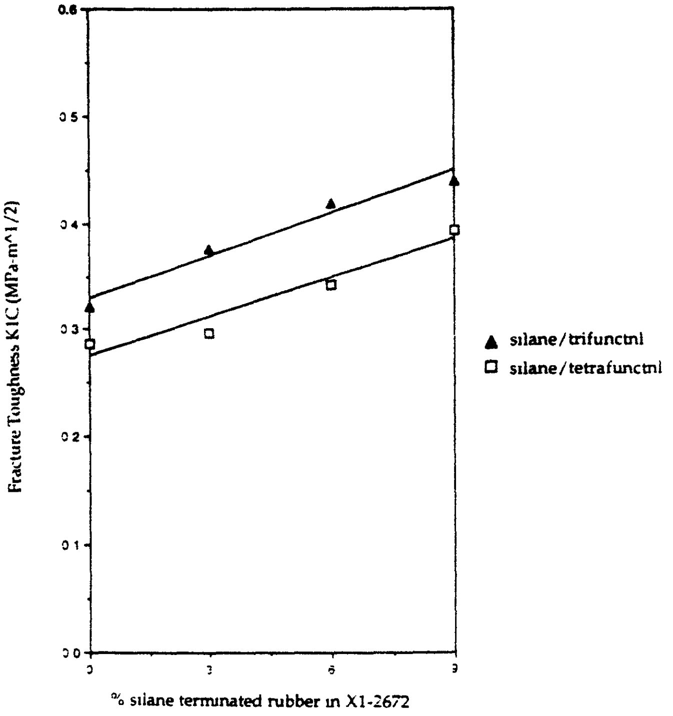


Figure 3.70: Variation of the average fracture toughness (K_{IC}) with rubber content for X1-2672™ castings with 0-9% silane terminated rubber (DP_n=4), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours.

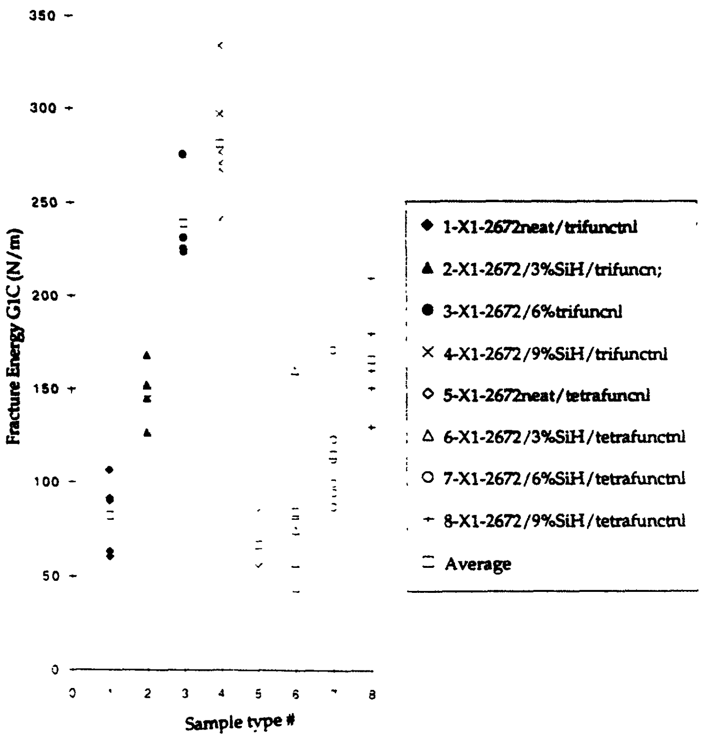


Figure 3.71: The fracture energy (G_{IC}) of X1-2672™ castings with 0-9% silane terminated rubber (DP_n=4), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours.

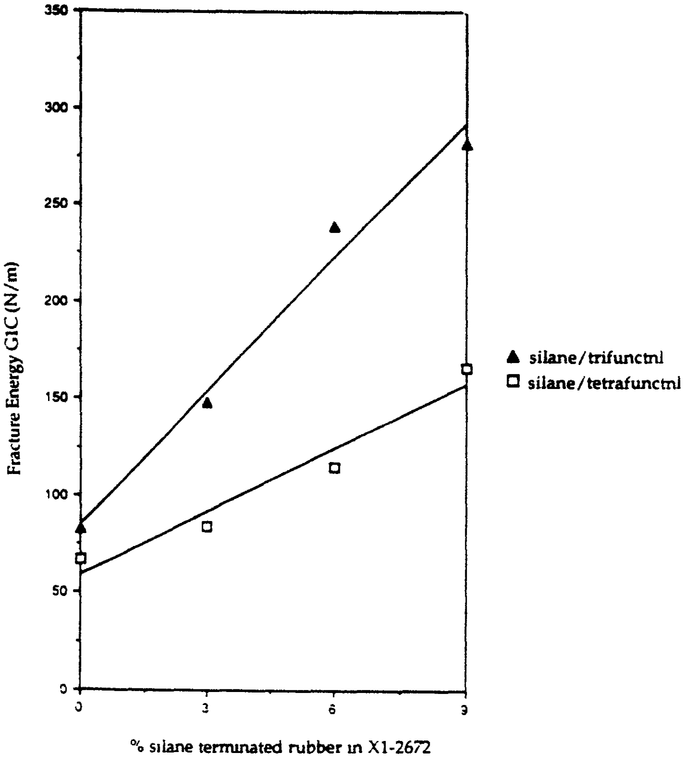


Figure 3.72: Variation of the average fracture energy (G_{IC}) with rubber content for X1-2672™ castings with 0-9% silane terminated rubber (DP_n=4), cured with tri and tetrafunctional cross-linkers and post-cured at 260°C/8 hours.

3.2 Scanning Electron Microscopy (SEM).

Figures 3.73 -3.75 show SEM micrographs of the fracture surfaces of X1-2672™ with 0 and 6% vinyl and silane terminated rubber cured with the trifunctional cross-linker and Figures 3.76-3.78 show 0 and 6% vinyl and silane terminated rubbers cured with the tetrafunctional cross-linker. All samples were cured at 160°C or 140°C for 16 hours and post-cured at 260°C for 8 hours.

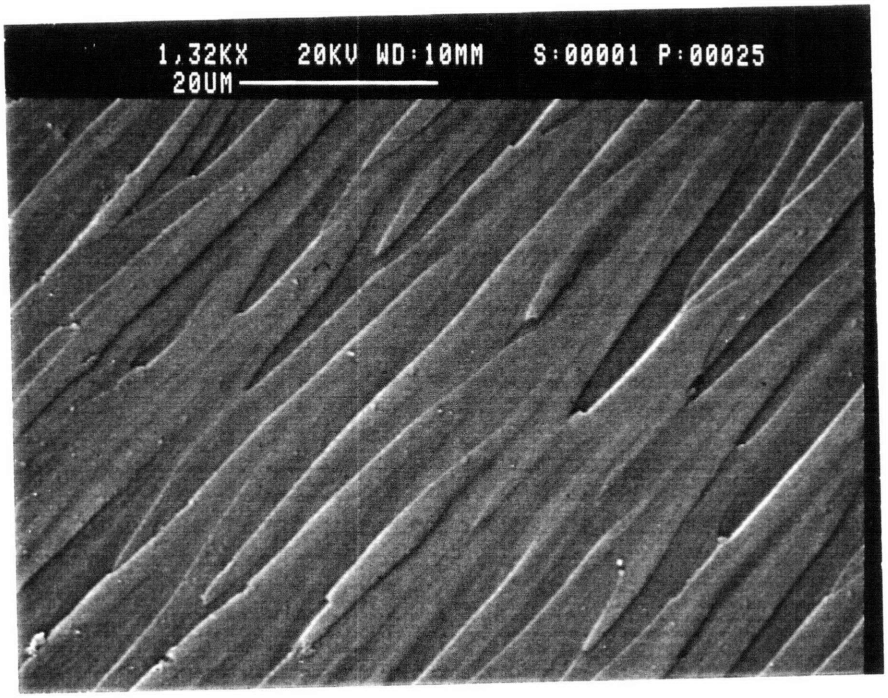


Figure 3.73: SEM micrographs at ~1.3 kX magnification of X1-2672™ neat resin cured at 160°C for 16 hours with the trifunctional cross-linker and post-cured at 260°C/8 hours.

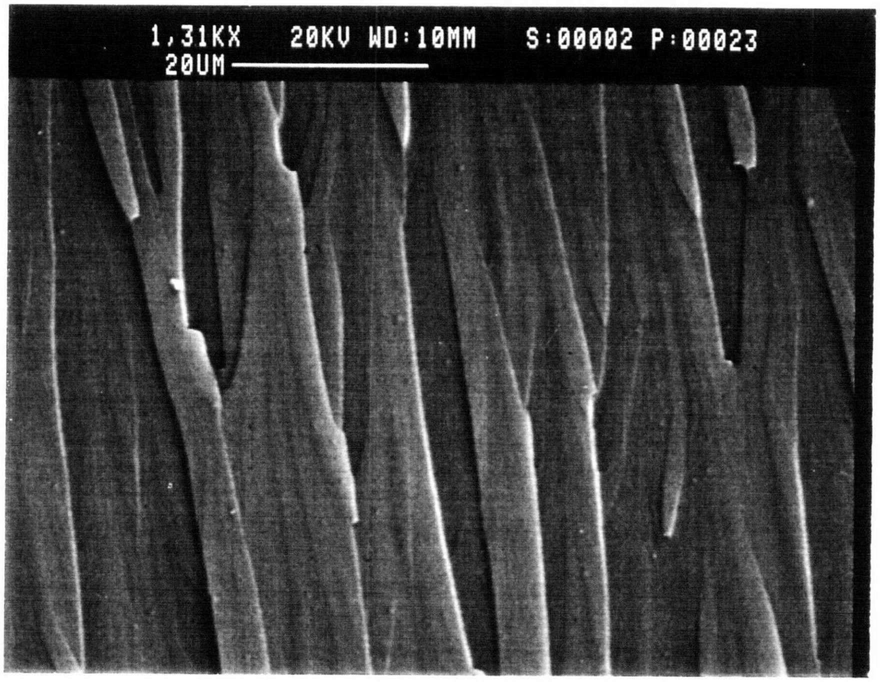


Figure 3.74: SEM micrographs at ~1.3 kX magnification of X1-2672™ resin with 6% vinyl terminated PDMS (DP_n=9), cured at 160°C for 16 hours with the trifunctional cross-linker and post-cured at 260°C/8 hours.

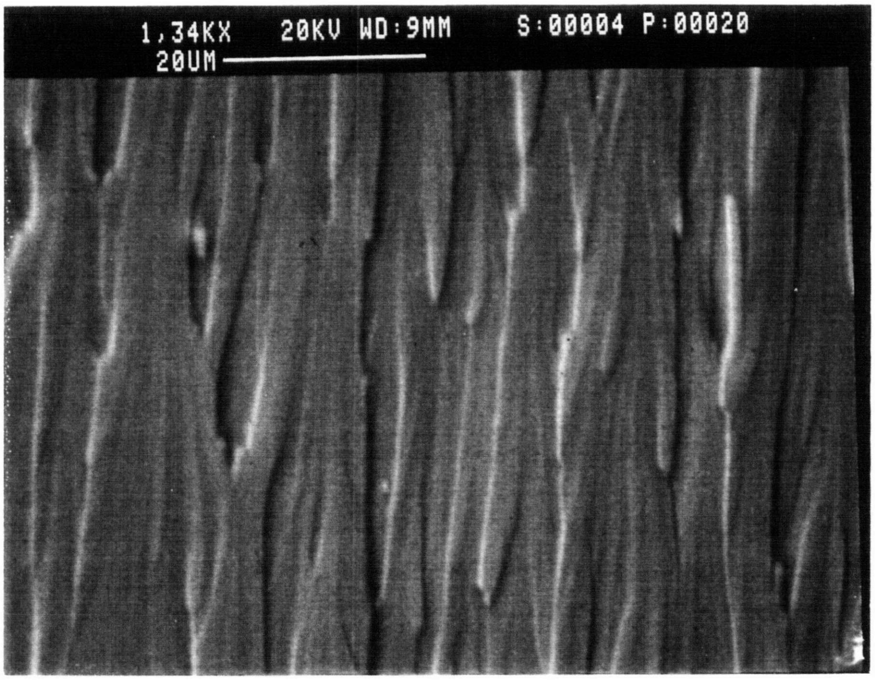


Figure 3.75: SEM micrographs at ~1.3 kX magnification of X1-2672™ resin with 6% silane terminated rubber (DP_n=4), cured at 160°C for 16 hours with the trifunctional cross-linker and post-cured at 260°C/8 hours.

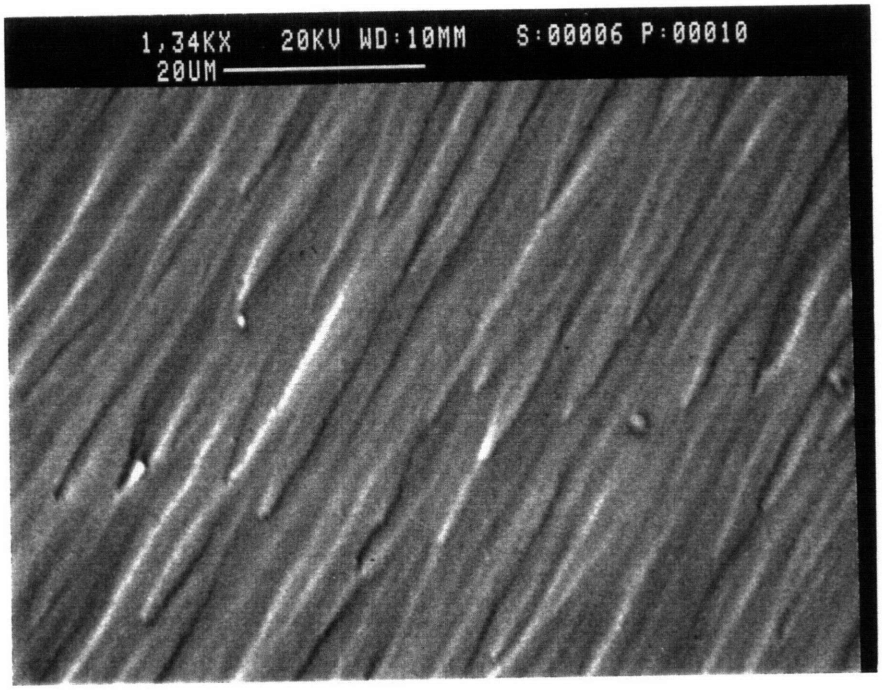


Figure 3.76: SEM micrographs at 1.3 kX magnification of X1-2672™ neat resin cured at 140°C for 16 hours with the tetrafunctional cross-linker and post-cured at 260°C/8 hours.

Figure 3.77: SEM micrographs at 1.3 kX magnification of X1-2672™ resin with 6% vinyl terminated PDMS (DP_n=9), cured at 140°C for 16 hours with the tetrafunctional cross-linker and post-cured at 260°C/8 hours.

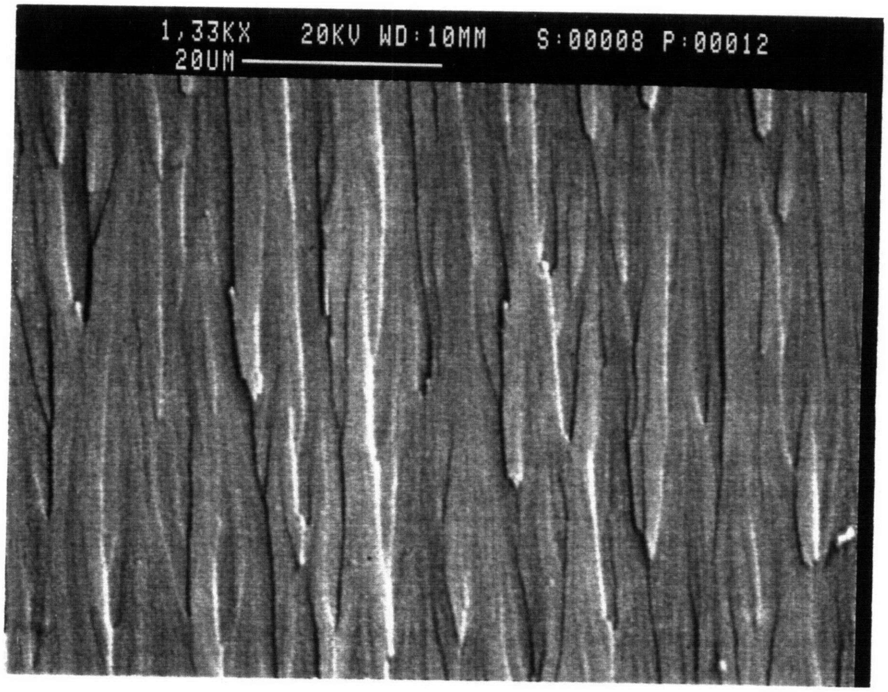


Figure 3.78: SEM micrographs at ~1.3 kX magnification of X1-2672™ resin with 6% silane terminated rubber (DP_n=4), cured at 140°C for 16 hours with the tetrafunctional cross-linker and post-cured at 260°C/8 hours.

3.3 Nuclear Magnetic Resonance (NMR)

Figure 3.79 - 3.81 shows ^{29}Si solid state NMR scan of X1-2672™ neat resin, X1-2672™ with 9% vinyl terminated PDMS and X1-2672™ with 9% silane terminated rubber respectively.

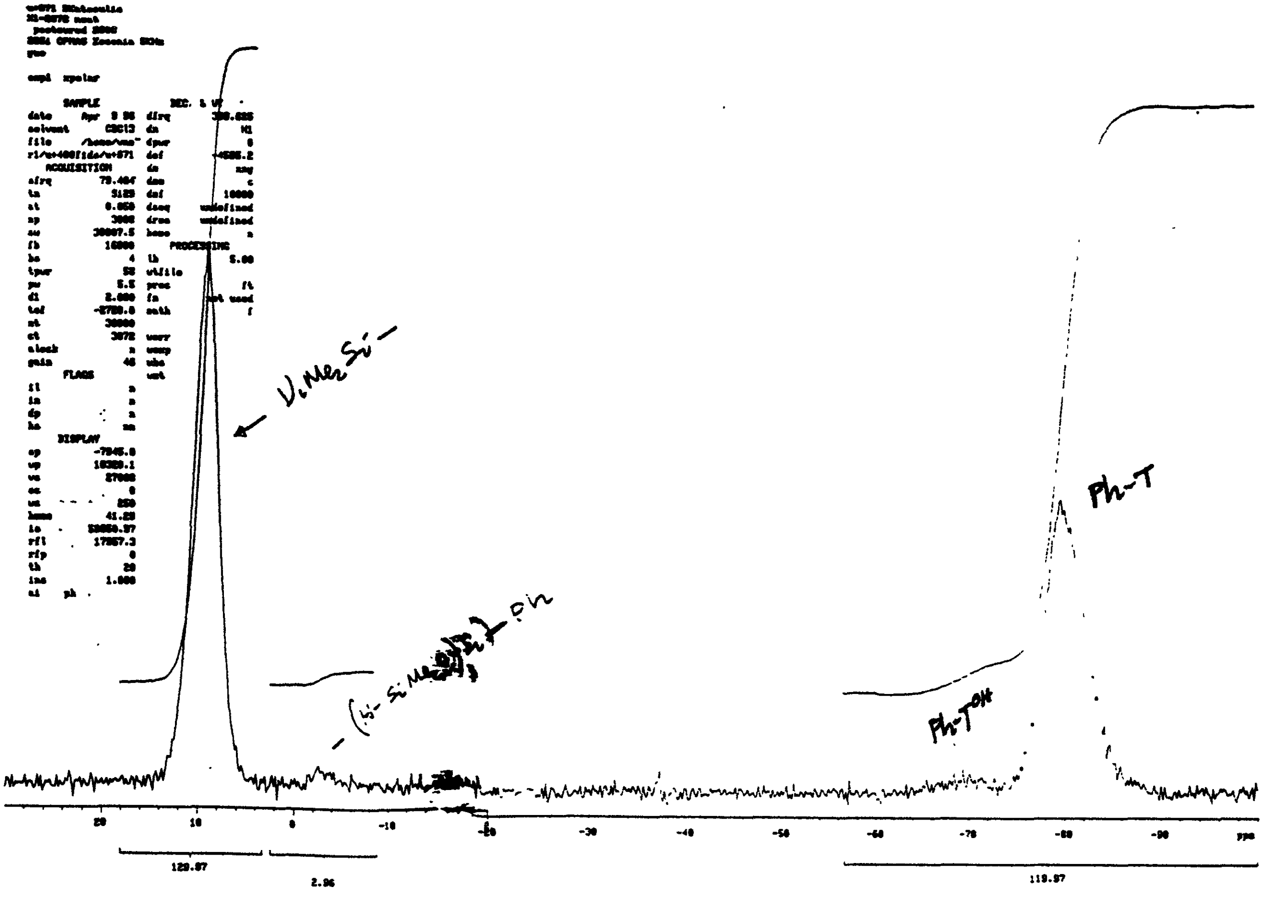
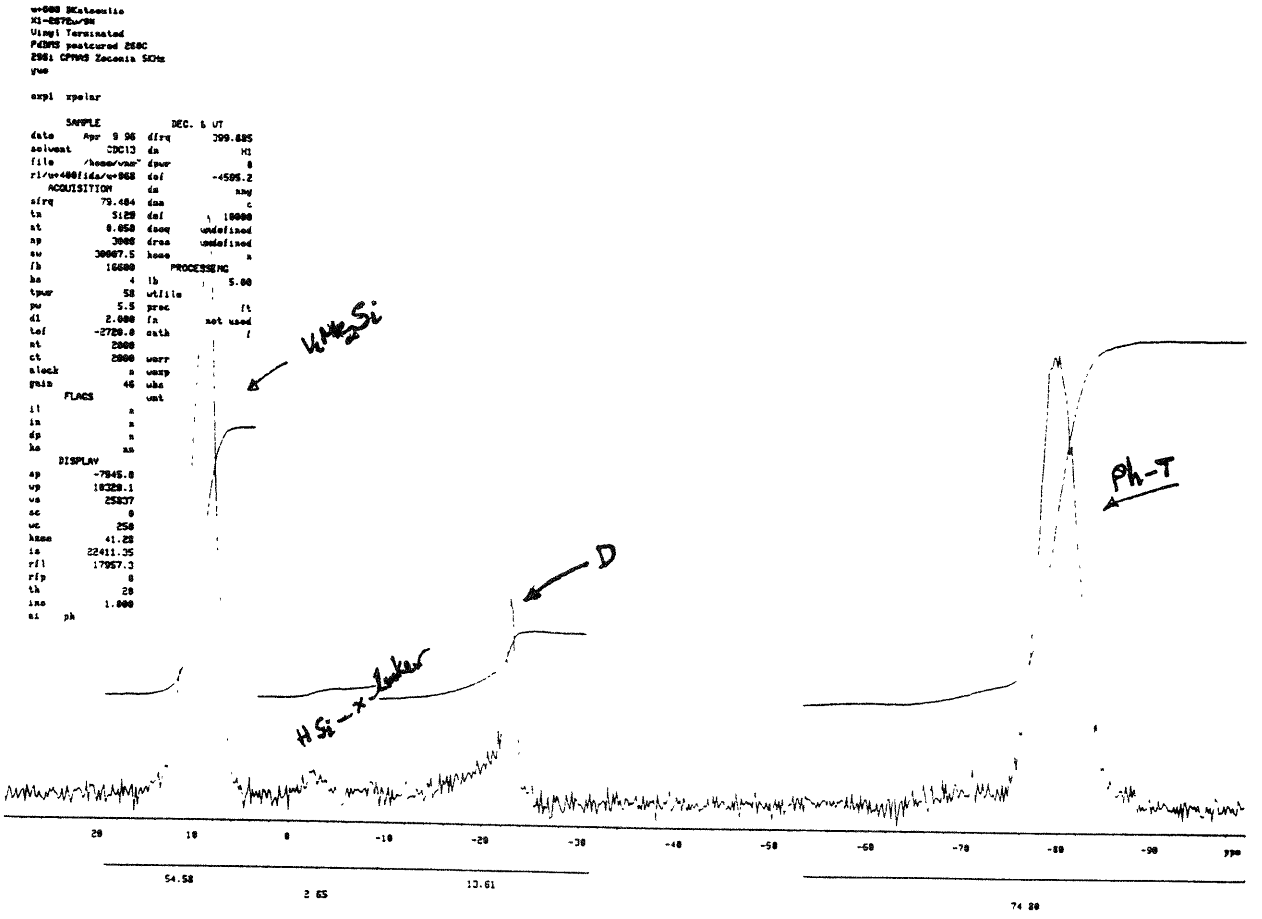


Figure 3.79: ^{29}Si solid state NMR scan of X1-2672™ neat resin cured with the trifunctional cross-linker and post-cured at 260°C/8 hours.

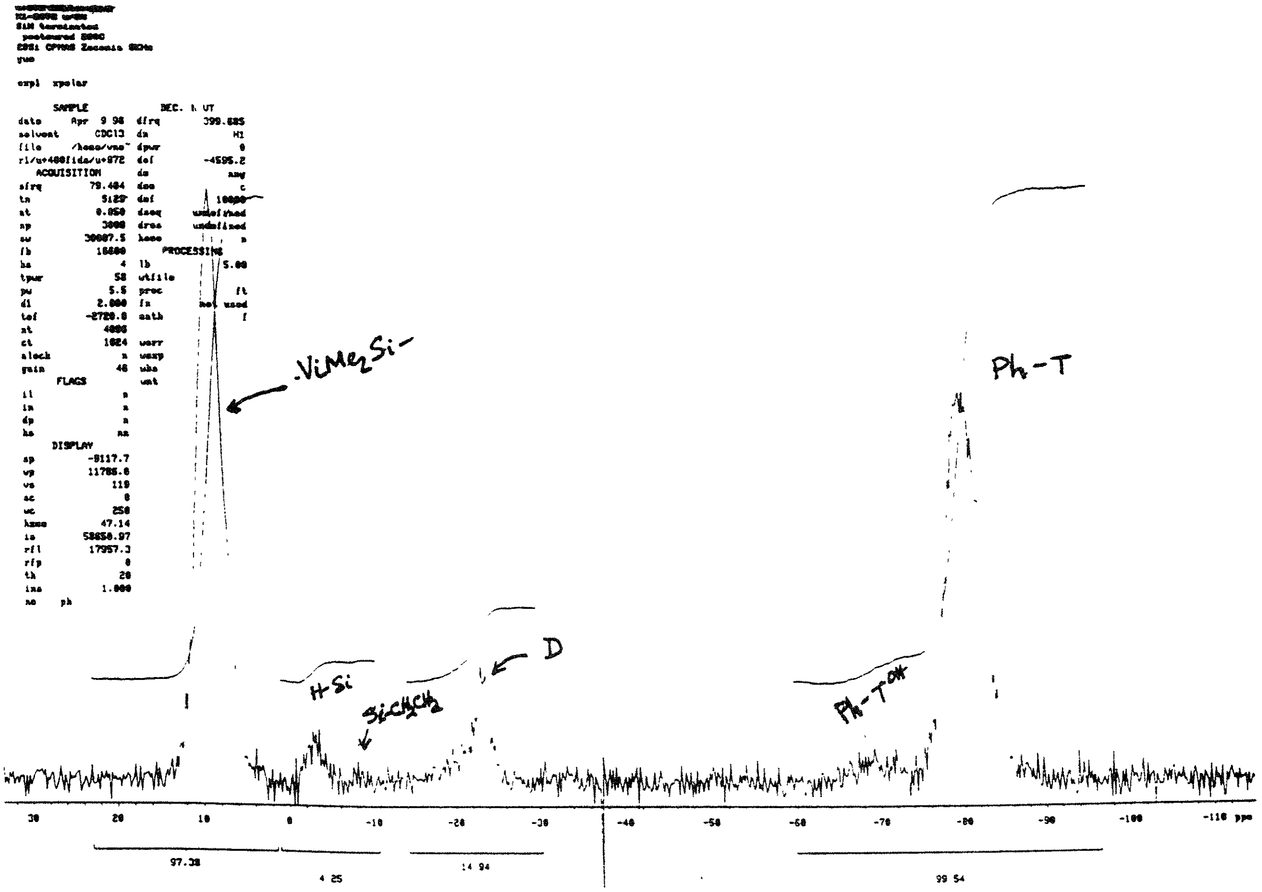


```
u+600 BKatsoulis
X1-2672w/9%
Vinyl Terminated
PdMS postcured 260C
29Si CPMAS Zeconia 5KHz
ywe

expl  xpolar

      SAMPLE                DEC. & VT
date      Apr  9 96  dfrq        399.885
solvent       CDC13  dn               H1
file     /home/vnmr  dpwr              0
ri/u+400fids/u+060   dof         -4505.2
   ACQUISITION       dm              nny
sfrq         79.484  dmm               c
tn             Si29  dmf           10000
at            0.050  dseq      undefined
np             3000  dres      undefined
sw          30007.5  homo              n
fb            16000       PROCESSING
bs                4  lb             5.00
tpwr             58  wtfile
pw              5.5  proc             ft
d1            2.000  fn         not used
tof         -2720.0  math              f
nt             2000
ct             2000  werr
alock             n  wexp
gain             46  wbs
      FLAGS          wnt
il                n
in                n
dp                n
hs               nn
     DISPLAY
sp          -7845.0
wp          10320.1
vs            25837
sc                0
wc              250
hzmm          41.28
is         22411.35
rfl         17957.3
rfp               0
th               20
ins           1.000
ai    ph
```

Figure 3.80: ^{29}Si solid state NMR scan of X1-2672™ resin with 9% vinyl terminated PDMS (DP_n=9), cured with the trifunctional cross-linker and post-cured at 260°C/8 hours.



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exp1  xpolar

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date     Apr  9 90  dfrq       399.885
solvent      CDCl3  dn              H1
file    /home/vno~  dpwr             0
ri/u+400fida/u+072  dof        -4595.2
   ACQUISITION      dm             nny
sfrq        79.484  dmm              c
tn            Si29  dmf          10000
at           0.050  dseq     undefined
np            3000  dres     undefined
sw         30007.5  homo             n
fb           16000       PROCESSING
bs               4  lb            5.00
tpwr            58  wtfile
pw             5.5  proc            ft
d1           2.000  fn        not used
tof        -2720.0  math             f
nt            4096
ct            1024  werr
alock            n  wexp
gain            46  wbs
      FLAGS         wnt
il               n
in               n
dp               n
hs              nn
     DISPLAY
sp         -8117.7
wp         11785.0
vs             119
sc               0
wc             250
hzmm         47.14
is        58658.97
rfl        17957.3
rfp              0
th              20
ins          1.000
nm      ph
```

Figure 3.81: ^{29}Si solid state NMR scan of X1-2672™ resin with 9% silane terminated PDMS (DP_n=4), cured with the trifunctional cross-linker and post-cured at 260°C/8 hours.

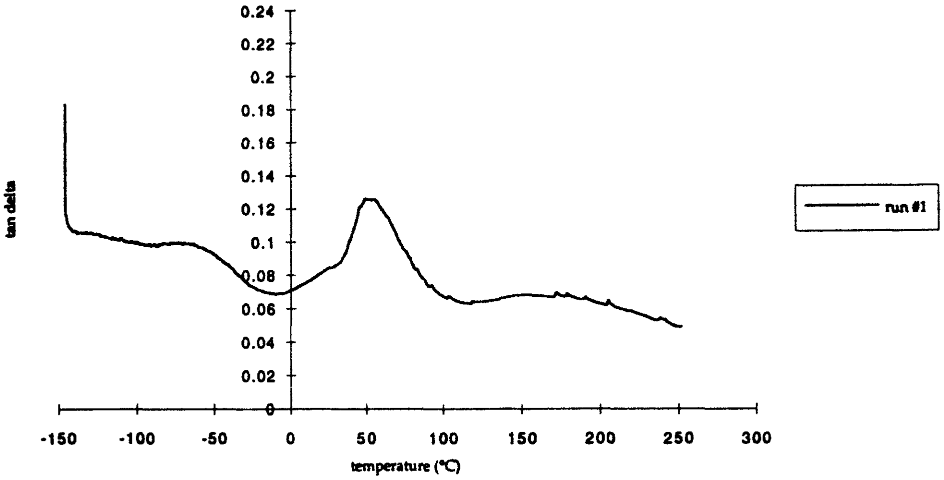
3.4 Dynamic Mechanical Analysis (DMA)

Each of Figures 3.82-3.83 show one DMA scan of the tan delta variations with temperature for the following samples:

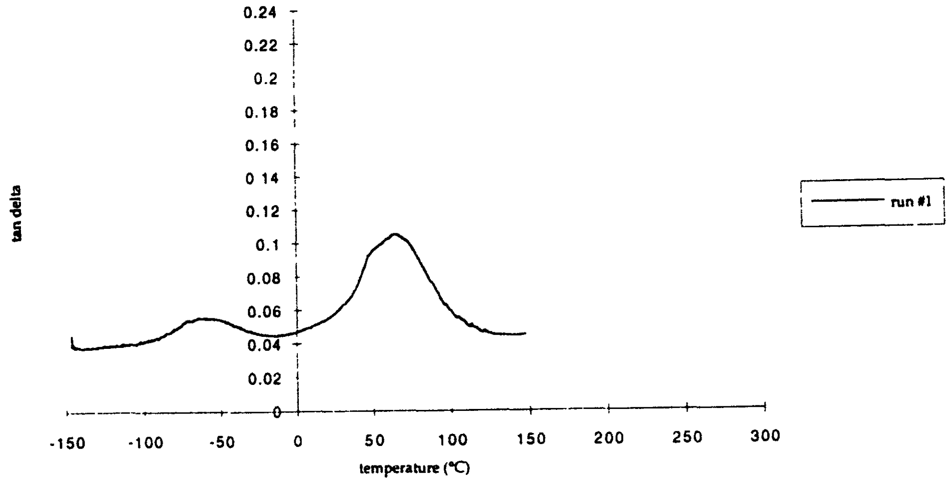
- X1-2672™ with 0,6 and 12% vinyl terminated PDMS (DP_n=9), cured at 160°C for 16 hours and post-cured at 260°C for 8 hours with the trifunctional cross-linker.
- X1-2672™ with 0,6 and 12% silane terminated rubber (DP_n=4), cured at 160°C for 16 hours and post-cured at 260°C for 6 hours with the trifunctional cross-linker.

The accompanying scans of the storage (E') and loss (E") moduli are shown in Appendices C-1 to C-4.

Tan delta of X1-2672 with 12% vinyl terminated PDMS cured with trifunctional cross-linker.



Tan delta of X1-2672 with 6% vinyl terminated PDMS cured with trifunctional cross-linker



Tan delta of X1-2672 neat resin cured with trifunctional cross-linker.

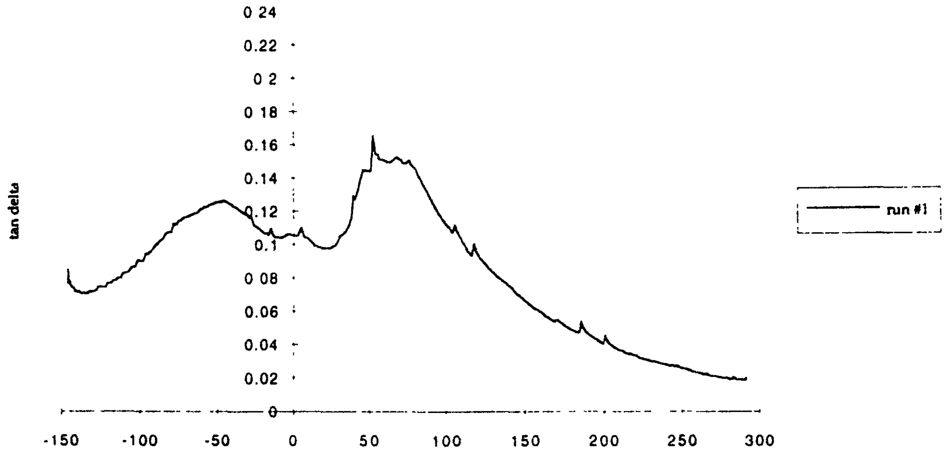
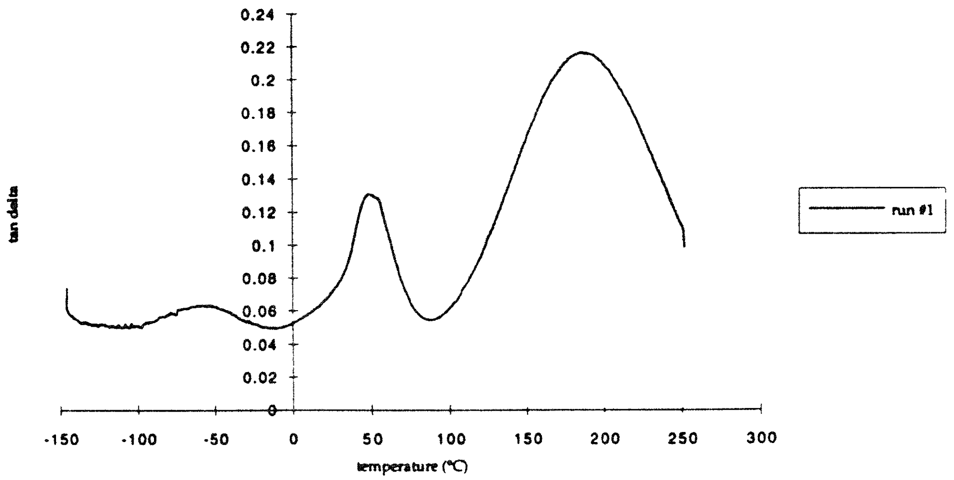
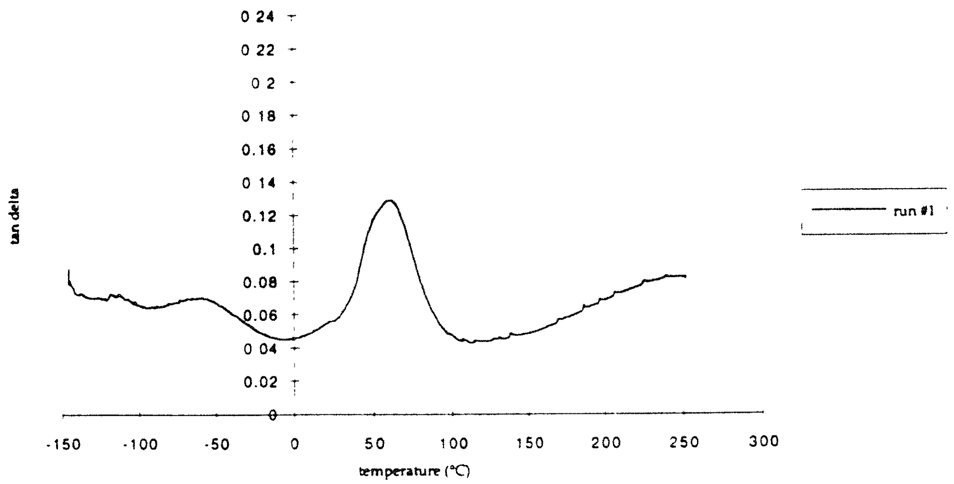


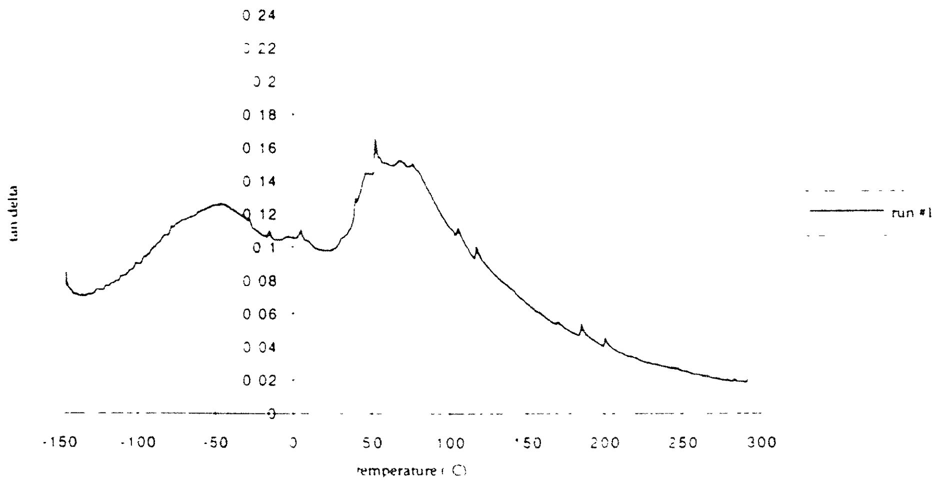
Figure 3.82: Tan delta variation with temperature, at a temperature rate of 2°C/min and a frequency of 5 Hz, of X1-2672™ with 0,6 and 12% vinyl terminated PDMS (DP_n=9) cured at 160°C/16 hours and post-cured at 260°C/8 hours with the trifunctional cross-linker.



Tan delta of X1-2672 with 12% silane terminated rubber cured with trifunctional cross-linker.



Tan delta of X1-2672 with 6% silane terminated rubber cured with trifunctional cross-linker.



Tan delta of X1-2672 neat resin cured with trifunctional cross-linker.

Figure 3.83: Tan delta variation with temperature, at a temperature rate of 2°C/min and a frequency of 5 Hz, of X1-2672™ with 0,6 and 12% silane terminated rubber (DP_n=4) cured at 160°C/16 hours and post-cured at 260°C/8 hours with the trifunctional cross-linker.

Chapter 4

Discussion

4.1 Mechanical Testing

4.1.1 Effect of Post-cure temperature and time on the mechanical properties of X1-2672™ containing vinyl and silane terminated rubbers.

The increase in the post-cure temperature and time from 200°C/4 hours to 260°C/8 hours resulted in an increase in the average flexural modulus and flexural strength for X1-2672™ resin with 0,3,6, and 9% vinyl terminated PDMS. This indicated that the initial post-cure conditions did not sufficiently cure the resin network. As a result, the castings cured at 260°C for 8 hours were stiffer - illustrated by higher moduli- and could also withstand higher stresses before breakage, evident by the increase in average yield strength values. The increase in stiffness as a result of the higher post-cure temperature and time was accompanied by lower strains before yield shown in Figures 3.5 and 3.6. However it must be noted that the average decrease in the strain with the change in the post-cure conditions was not more than 1.5% and therefore not significant.

There was more of a decreasing trend in the toughness (energy to break), shown in Figures 3.7 and 3.8, when the post-cure temperature was increased to 260°C /8 hours, because these stiffer castings underwent less deformation and required less energy to break than those samples post-cured at 200°C for 4 hours.

The fracture toughness values shown in Figures 3.9 and 3.10, did not change significantly between the 200°C/4 hour and 260°C/8 hour post-cure conditions. For the castings post-cured at 200°C/4 hours the average fracture toughness values were 0.321,0.333, 0.328 and 0.300 MPa-m$^{1/2}$ for X1-2672™ with 0,3,6 and 9% vinyl terminated PDMS ; and 0.296, 0.320, 0.325 and 0.368 MPa-m$^{1/2}$ for the 0,3,6, and 9% vinyl rubber-containing castings post-cured at 260°C/8 hours.

The fracture energy comparison and average trends shown in Figures 3.11 and 3.12 was an amplification of the fracture toughness trend due to the squared relationship between the fracture energy and fracture toughness. The average fracture energy demonstrated upward trends from 100 to 143 N/m for the 200°C /4 hour post-cure and from 82 to 183 N/m for the 260°C /8 hour post-cure between 0% and 9% vinyl terminated rubber content. The upward trend of the fracture energy displayed by both sets of samples was not due to a significant increase in the fracture toughness with increasing rubber content. It was caused by the decrease in the modulus with increasing vinyl rubber content.

The silane samples post-cured at 200°C/ 4 hours and those post-cured at 260°C/ 8 hours both demonstrated a decrease in the modulus with increasing rubber content. Figures 3.13 and 3.14 also show no significant variation in the modulus between the two different post-cure conditions which indicates that the higher post-cure temperature and longer times did not have much effect.

The yield stresses in Figures 3.15 and 3.16 show slight decreases with increasing rubber content for the samples with silane terminated rubber post-cured under both conditions but there is little difference between the two curves.

The average yield strains for the samples under both post-cure conditions increase with increasing rubber content. This is shown in Figures 3.17 and 3.18. The difference between the two curves is approximately 1%, which is not great.
The toughness data shown in Figures 3.19 and 3.20 are quite similar. In general there is an increase in the energy to break with increasing rubber content but the effect of post-cure temperature is small.

Figures 3.21 and 3.22, the samples post-cured at 200°C /4 hours display an increase in the fracture toughness from 0.321 to 0.44 MPa-$m^{1/2}$ with increasing rubber content. The samples post-cured at 260°C /8 hours also show an increase in the fracture toughness and the average values are slightly higher. The average varied from 0.296 to 0.482 MPa-$m^{1/2}$ which is approximately a 25% increase. While the difference in the values for the two post-cure conditions is not large, the silane terminated rubber toughened the resin much more than the vinyl terminated rubber.

The increasing fracture toughness of the samples coupled with the moderate decrease in the stiffness with increasing rubber content resulted in significant increases in the fracture energy for the 200°C/4 hour and the 260°C/8 hour samples: the fracture energy values are shown in Figures 3.23 and 3.24. The average for the 200°C /4 hour samples varied from 99.6 to 234 N/m for 0 to 9% silane terminated rubber. The values for the 260°C/8 hour samples were higher generally, going from 82.3 N/m for the neat resin to 281.4 N/m for the sample containing 9% silane terminated rubber. This is an increase in the crack propagation resistance of approximately 3.5 times the neat resin average when 9% silane terminated rubber is reacted into the resin. The sample containing 9% silane terminated rubber post-cured at 200°C/4 hours displayed an increase of approximately 2 times the neat resin value.

The trends demonstrated by the samples containing both types of rubber under both post-cure conditions show the silane terminated rubber is more effective in toughening the resin matrix than the vinyl terminated. The change in the post-cure conditions did not result in significant changes for most of the mechanical properties particularly in those samples containing the vinyl terminated rubber. For the silane terminated rubber it was clear that the increase in the post-cure temperature and time resulted in higher values of fracture toughness and energy. It is for this reason that the post-cure temperature and time of 260°C and 8 hours were used for the following experiments in which the effect of rubber content between 0 and 15% for both rubber additives was evaluated. The results of the flexural and fracture toughness testing of these samples are shown in Figures 3.25-3.48.

4.1.2 Effect of rubber content on the mechanical properties of X1-2672™ resin containing 0-15% vinyl and silane terminated rubbers, post-cured at 260°C for 8 hours.

Figures 3.25 and 3.26 show the variation of the flexural modulus with vinyl terminated rubber content. The stiffness of the castings decreased with increasing rubber content. The average stiffness varied from 156.4 ksi for the neat resin sample to 79.6 ksi for the sample containing 15% vinyl terminated rubber. This is a 50% reduction in the modulus.

As seen in Figures 3.27 and 3.28, the yield strength also decreased by about 40% with increasing rubber content, from 3645 psi for the neat resin to 2191 psi for the samples containing 15% rubber.

The yield strains, shown in Figures 3.29 and 3.30, increased with rubber content as the rubber produced a more deformable casting. The strains varied from 3.4% for the neat resin to 5% for the resin casting containing 15% rubber.

For the toughness values shown in Figures 3.31 and 3.32 there is so much scatter that a trend is not evident. The average values for the toughness were 8.28, 11.04, 10.6, 12.6, 15.6 and 15.4 lb-in/in^3 for the samples containing 0,3,6,9,12, and 15% vinyl terminated PDMS.

The fracture toughness values are shown in Figures 3.33 and 3.34. There is a moderately increasing trend with increasing rubber content.

Figures 3.35 and 3.36, the fracture energy show more of an increase, reflecting the decrease in modulus. It seems that the vinyl terminated rubber did not toughen the resin very much.

Figures 3.37 and 3.38 show the variation of the modulus with silane rubber content. Similar to the vinyl terminated PDMS, the silane terminated rubber showed a 50% decrease in the modulus, but their values were higher then the vinyl terminated ones.

Figures 3.39 and 3.40, a 20% decrease in the yield stress is seen. In comparison to the samples containing the vinyl terminated PDMS, the silane samples had higher yield stress values and a smaller decrease as the rubber content increased.

Figures 3.41 and 3.42 show the yield strain variation with silane rubber content. It increases substantially, more so than with the vinyl terminated rubber, despite the higher DP_n in the latter. This suggests the silane rubber was better able to penetrate the resin network than the vinyl terminated PDMS.

The variation of the toughness with rubber content is shown in Figures 3.43 and 3.44. For the silane samples there was an increase in the toughness with increasing rubber content.

In Figures 3.45 and 3.46, the silane samples show an increase in the average fracture toughness. The average values rise from 0.296 to 0.502 MPa-$m^{1/2}$. The numbers indicate that the silane rubber toughens about twice as effectively as the vinyl.

The fracture energy is shown in Figures 3.47 and 3.48. In comparison to the vinyl terminated samples, the silane terminated rubber produced much higher fracture energy values. The higher values indicate the silane rubber is better able to affect the network than the vinyl terminated rubber. Possibly this is because the silane rubber can react directly with the vinyl groups on the resin. The vinyl terminated rubber only can react with the silane groups on the cross-linker which may decrease the likelihood of penetrating the resin network.

4.1.3 Effect of cross-linker functionality on the mechanical properties of X1-2672™ resin containing vinyl and silane terminated rubbers, post-cured at 260°C for 8 hours.

Figures 3.49 to 3.60 show the comparison between X1-2672™ samples containing 0-9% vinyl terminated PDMS cured with tri and tetra-functional cross-linkers. Figures 3.49 and 3.50 show the variation of the modulus. The modulus increases when the functionality is increased from 3 to 4, however as the rubber content increases the values for the two cross-linkers converge.

The yield stress values are shown in Figures 3.51 and 3.52. The average yield strength values for the samples cured with the tetrafunctional cross-linker displayed a larger decrease than the samples cured with the tri-functional cross-linker, but generally the difference is small.

The yield strain values are shown in Figures 3.53 and 3.54. They decreased with the increase in the cross-linker functionality. For those samples cured with the trifunctional cross-linker, the yield strains increased from 3.4 to 4.7% between the neat resin and the samples containing 6% vinyl terminated PDMS, followed by a decrease to 4% strain for the 9% sample. The samples that were cured with the tetrafunctional cross-linker displayed lower yield strains, on average, due to the increase in the cross-link density of the resin network, but there was little variation with increasing rubber content. The average yield strains for the samples cured with the tetrafunctional cross-linker were 3.1,3.1,2.5 and 3.5% elongation for the neat resin, 3, 6, and 9% vinyl terminated rubber. It was expected that the strains should have increased with increasing rubber content and the reason for not doing so is unclear.

The energy to break values are shown in Figures 3.55 and 3.56. Again, it is not understood why the peak exists in one curve and the decrease is present in the other. Possibly internal defects were present in the samples but this is simply conjecture.

Figures 3.57 and 3.58 show the comparison of the fracture toughness. The samples cured with the trifunctional cross-linker, are somewhat higher than the tetrafunctional ones and both increase with increasing rubber content. The data are consistent with expectations.

The fracture energy values are shown in Figures 3.59 and 3.60. Both sets of samples show an increase with increased rubber content. The values for the samples with the tetrafunctional cross-linker are lower than with the trifunctional one. The increase shows an improved ability to resist crack propagation but the values are still low compared to epoxy resins, which typically are in the range of 400 N/m.

Figures 3.61 and 3.62 show the flexural moduli for X1-2672™ containing silane terminated rubber, cured with trifunctional and tetrafunctional cross-linkers. It is seen that the values are lower for the samples cured with the trifunctional cross-linker, which is consistent with a higher cross-link density in the tetra-functional system. Also the modulus values for the silane rubber are higher the for the vinyl one.

The yield stress is presented in Figures 3.63 and 3.64. It decreases with rubber content and there is not much effect of the cross-linker. These samples had higher yield stresses than the samples containing the vinyl terminated PDMS.

The yield strain values in Figures 3.65 and 3.66 show higher increases rubber content for the samples cured with the trifunctional cross-linker. This is consistent with the more highly cross-linked structure to be expected with the tetrafunctional material.

The work to break values in Figures 3.67 and 3.68 are quite interesting. The trifunctional cross-linker produces a more open structure, more responsive to rubber flexibilization. In contrast, the other system is remarkably unresponsive to rubber additions; apparently it is too closed to benefit from them.

The fracture toughness values, shown in Figures 3.69 and 3.70 contradict this. Both samples increase with rubber content and the trifunctional cross-linker has the higher average values. Perhaps this parameter is a more sensitive indicator of network density than many of the others. Such would be inferred from Figures 3.71 and 3.72 where the crack resistance increases strongly with rubber content, and in a consistent manner.

The results for the samples with vinyl and silane terminated rubber cured with both cross-linker types showed that, although samples cured with the tetrafunctional cross-linker were stiffer, the trifunctionsl cross-linker was better able to produce a network which is stiff but not as brittle. The stiffness for the samples containing vinyl terminated PDMS increased by 3-15% with an increase in the cross-linker functionality from 3 to 4; while in the samples with the silane terminated rubber, the moduli increased 12-15% by increasing the cross-linker functionality from 3 to 4. In summary, the tetrafunctional cross-linker produced a lower resistance to crack initiation and propagation which could not be compensated with rubber modification up to 9% content.

4.2 Scanning Electron Microscopy (SEM)

Following the mechanical testing, all the samples underwent Scanning Electron Microscopy (SEM) to evaluate the differences in the fracture surfaces between the X1-2672™ neat resin and the rubber modified samples. Figures 3.73-3.75 show micrographs of 0 and 6% rubber modified samples cured with the trifunctional cross-linker at 160°C for 16 hours and post-cured at 260°C for 8 hours.

The neat resin sample showed parallel cracks on the fracture surface, some of which bifurcated in the notch direction. In comparison, the sample with 6% vinyl terminated PDMS shown in Figure 3.74 and with 6% silane terminated rubber shown in Figure 3.75, there are no significant differences between them.

It was expected that with rubber modification, there would be changes in the failure mechanism, observable by SEM. Examples of such changes include the development of localized regions of plastic flow (plastic zone development), or presence of voids due to possible rubber cavitation. However, there was no evidence of plasticity of the matrix. With the addition of either rubber type in the resin matrix, the mode of failure was still brittle.

Figures 3.76-3.78 show the neat resin and 6% rubber modified samples cured with the tetrafunctional cross-linker. From the mechanical testing results it was shown that these matrices were more brittle than those cured with the trifunctional one. It was observed from Figure 3.76 that the neat resin cured with tetrafunctional cross-linker fractured in a brittle manner. The cracks are also oriented parallel to each other and show bifurcation in the notch direction.

The fracture surface of this sample looked no different from the neat resin one cured with the trifunctional cross-linker. For those samples modified with 6% vinyl and silane terminated rubbers in Figures 3.77 and 3.78 respectively, there was no change in the fracture mode. The fracture was still brittle and the surfaces appeared similar to those cured with the trifunctional cross-linker.

From the mechanical testing results, it was indicated that the rubbers - particularly the silane terminated rubbers - produced changes in the fracture toughness and fracture energy values. However these changes did not change the failure mode from a brittle to ductile. There may have been other changes in the mechanism of interaction between the rubber and the crack tip, however it appears that a tool higher in resolution than SEM may be necessary to make such observations.

4.3 Nuclear Magnetic Resonance (NMR)

^{29}Si solid state NMR was carried out on X1-2672™ neat, X1-2672™ with 9% vinyl terminated PDMS and X1-2672™ with 9% silane terminated rubber to quantify the reactivity of the resin with the cross-linker and rubbers. Figure 3.79 shows that unreacted vinyl groups ($ViMe_2Si$) are in the resin network at a chemical shift of 10 ppm. Unreacted vinyl groups were also detected in the samples modified with 9% vinyl and 9% silane terminated rubbers. This is shown in Figures 3.80 and 3.81 respectively.

These scans indicate that the resin was not fully reacted with the cross-linker nor was it fully reacted with the rubbers. This may be the reason that the samples modified with the vinyl terminated PDMS showed little variation of the fracture toughness with rubber content.

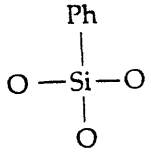
The silane rubber modified samples show an increase of fracture toughness with increasing rubber content despite the significant quantity of unreacted vinyl groups on the resin. This suggests that the silane rubber reacted with some of the vinyl groups in the resin, more so than the vinyl terminated PDMS. This is shown by the presence of a $SiCH_2CH_2$ peak (the hydrosilylation bond) at a chemical shift of ~-8 ppm in Figure 3.80.

It was not certain why there were large quantities of unreacted vinyl groups. Possible reasons include side reactions in the system, such as the hydrolysis of the silane groups on the cross-linker by water introduced in the system by the platinum catalyst solution. The platinum catalyst in isopropanol is very hygroscopic and even though degassing was carried out on the system after addition of the platinum catalyst, the amount of solvent removed was not necessarily complete.

Hydrolysis of the silane groups on the cross-linker is also favored at elevated temperature in the presence of oxygen which is the condition of cure in an air oven. The hydrolysis of the cross-linker would result in the formation of silanol which in turn can react with itself further to form Si-O-Si bonds. This may be the peak designated "D" on the NMR scan ("D" refers to O-Si-O groups) at a chemical shift of -25 ppm in Figures 3.80 and 3.81. It is uncertain why the "D" peak was not present in the neat resin scan.

4.4 Dynamic Mechanical Analysis (DMA)

DMA was another tool used to observe the effect of rubber modification. Figure 3.82 shows the variation of tan delta with temperature at a rate of 2°C /min and a frequency of 5 Hz for X1-2672™ with 0,6 and 12% vinyl terminated PDMS. These runs show that the neat resin has two characteristic transitions: an alpha (α) transition at about +63°C and a beta (β) transition at approximately -50°C. The high temperature peak has a width at half maximum over a 110 degree range and the low temperature peak has a width at half -maximum over a 100 degree range. Both peaks are associated with the phenyl T



$\mathrm{O-\overset{\overset{Ph}{|}}{\underset{\underset{O}{|}}{Si}}-O}$

transition.

It was observed that the addition of 6% vinyl terminated PDMS caused a slight narrowing of the α tan delta peak and a decrease in the level of the peak to 0.1. A broadening of the β tan delta peak at a level of 0.06 is also shown. Adding 12% vinyl rubber caused further narrowing of the α tan delta peak to a width at half-maximum over a temperature range of 75 degrees and a more broad β peak over a range of 150 degrees.

In general, the narrowing of tan delta peaks indicates an increase of phase separation, so the narrowing of the α resin peak was possibly due to segregation of unreacted resin instead of well linked, dispersed chains. The increased broadening of the β peak over lower temperatures with increasing vinyl rubber content was probably due to the increased quantity of PDMS which has a glass transition at -125°C.

The increased rubber content should typically produce increased flexibility of the resin network shown by increased height of the tan delta peak. This trend was not present and this was probably involved the extent of reaction between the vinyl groups in the resin, and the cross-linker and rubber. Due to this unreactivity, no conclusions can be derived from the tan delta peaks until reproducible DMA runs of each sample are obtained.

Figure 3.83 show the variation of tan delta with temperature at a rate of 2°C /minute and a frequency of 5 Hz for X1-2672™ with 0,6 and 12% silane terminated rubber cured with trifunctional cross-linker. The incorporation of 6% silane terminated rubber caused the narrowing of the α peak; and the formation of a small low temperature peak at about -116°C - in addition to the -50°C resin β peak. There was also another high temperature peak at +250°C.

The addition of 12% silane terminated rubber resulted in three well defined peaks: a more narrow α resin peak, the β resin peak at about -50°C and a prominent high temperature peak at about 180°C. The narrowing of the α peak was possibly due to the increased formation of phase separated domains from the reaction of the silane terminated rubber with some of the resin. The development of the very high temperature peak was probably due to a glass transition of the Si-C bond, formed from the reaction between the silane rubber and the vinyl groups.

In general, it was observed that the silane terminated rubber caused greater changes in the transitions than the vinyl terminated rubber.

4.5 Discussion of Experimental Error

For the processing of the castings the source experimental error was not being able to accurately quantify the initial and final amount of solvents in each casting. The solvents were toluene from the resin solution, and isopropanol and water from the hygroscopic hexachloroplatinic acid solution. The amount of solvent removed varied between 3 -10 grams for each casting processed. This variation could have caused differences in the extent of cure particularly since there was the possibility of side reactions dominating the hydrosilylation cure .

Most of the analyses was the mechanical testing in which 6 samples were to be tested from each casting. However due to difficulty of machining the samples, the number of samples for some castings fell short of this number. It was also recommended that after machining, the edges of the mechanical testing samples should be polished - especially for the fracture toughness evaluations which are sensitive to the presence of laws. However at the very beginning, samples were not polished - this was quickly rectified but the results of unpolished samples were still used.

For the DMA, reproducible scans have to be carried out to determine the extent of experimental error for this apparatus.
To the best of our knowledge, the other errors from the other measurements (e.g. dimensional measurements and oven temperature control during cure) were negligible.

Chapter 5

Conclusions and Recommendations

A number of deductions can be made about how to improve the integrity of rubber modified X1-2672^{TM} resin.

The mechanical testing data indicated that the silane terminated rubber had more of an effect on the resin than the vinyl terminated. This was evident in the increases in the fracture toughness and fracture energies. The vinyl terminated PDMS caused little variation of the fracture toughness, but did cause a greater decrease in the stiffness with increasing rubber content than the silane rubber.

The differences in mechanical properties between the two rubbers could be due to a number of factors including a difference in reaction with the resin matrix i.e. chemical functionality, and a difference in the degrees of polymerization.

The NMR scans also show that the resin was not fully reacting with the trifunctional cross-linker and the rubbers. The diminished reaction between the resin and rubber may explain the absence of effects on the matrix by the vinyl terminated PDMS. However the silane terminated rubber additive, despite the presence of unreacted resin, appears to react with the resin to a greater extent than the vinyl terminated one.

The DMA data suggest the vinyl terminated PDMS may have had little effect on the matrix, despite the narrowing of the tan delta peaks with increasing rubber content. There was no separate rubber peak; only the broadening of the low temperature resin peak. The data also show that the silane terminated rubber had a greater effect on the resin by the development of a prominent high temperature loss peak.

Neither rubber changed the mechanism of fracture from brittle to ductile; the brittle character of the resin persisted.

Recommendations to improve the effects of the rubber modification include:

- the promotion of the reactivity of the resin by increasing the concentrations of cross-linker and/or platinum catalyst.
- establishing if the platinum catalyst may be the source of side reactions to the hydrosilylation cure due to its hygroscopic nature.
- curing the castings under nitrogen instead of air to reduce the side reactions of the cross-linker.
- evaluating the effect of chemical functionality and degrees of polymerization of the rubber additive.
- continuing to use DMA to analyze the effects of rubbers on the resin.
- using other tools to elucidate the morphology and fracture surfaces of the castings.

Appendix A

Reagent	Amount Required	Amount of trifunctional cross-linker
X1-2672 (75% soln in toluene)	68 grams	
Hexachloroplatinic Acid	1.51 mL	
Vinyl terminated PDMS		
0%	0 g	11.62 g
3%	1.53 g	12.10 g
6%	3.06 g	12.58 g
9%	4.59 g	13.05 g
12%	6.12 g	13.53 g
15%	7.65 g	14.01 g

Figure A-1: Formulations for X1-2672™ castings with the trifunctional cross-linker and vinyl terminated PDMS (DP_n=9).

Reagent	**Amount Required**	**Amount of trifunctional cross-linker**
X1-2672 (75% soln in toluene)	68 grams	
Hexachloroplatinic Acid	1.51 mL	
1,13,3,5,5,7,7 octamethyltetrasiloxane		
0%	**0g**	11.62 g
3%	**1.53 g**	10.43g
6%	**3.06 g**	9.25 g
9%	**4.59 g**	8.04 g
12%	**6.12 g**	6.87 g
15%	**7.65 g**	5.68 g

Figure A-2: Formulations for X1-2672™ castings with the trifunctional cross-linker and 1,1,3,3,5,5,7,7 octamethyltetrasiloxane (DP_n=4).

Reagent	Amount Required	Amount of tetrafunctional cross-linker
X1-2672 (75% soln in toluene)	68 grams	
Hexachloroplatinic Acid	1.51 mL	
vinyl terminated PDMS		
0%	0 g	8.45 g
3%	1.53 g	8.78 g
6%	3.06 g	9.20 g
9%	4.59 g	9.43 g

Figure A-3: Formulations for X1-2672™ castings with the tetrafunctional cross-linker and vinyl terminated PDMS (DP_n=9).

Reagent	Amount Required	Amount of trifunctional cross-linker
X1-2672 (75% soln in toluene)	68 grams	
Hexachloroplatinic Acid	1.51 mL	
1,13,3,5,5,7,7 octamethyltetrasiloxane		
0%	0 g	8.45 g
3%	1.53 g	7.59 g
6%	3.06 g	6.72 g
9%	4.59 g	5.86 g

Figure A-4: Formulations for X1-2672™ castings with the tetrafunctional cross-linker and 1,1,3,3,5,5,7,7 octamethyltetrasiloxane (DP_n=4).

Time Taken (hrs.)	Initial Temp.- Final Temp. (°C)
1.5	room temp. - 100
1.0	100 - 110
1.0	110 - 120
1.0	120 - 135
1.0	135-140
16 hour cure	140

Figure A-5: The temperature ramp used to achieve minimal cracking for X1-2672™ castings cured with the tetrafunctional cross-linker.

Appendix B

Appendix B

X1-2672 neat/ unpost-cured	Yield Stress (psi)	Yield strain(in/in)	Modulus (ksi)	Toughness (inlb/in3
	3905	0.0592	142.4	17.12
	3814	0.0699	109	19.87
	3283	0.0485	127.4	11.55
	3363	0.0549	122.8	13.73
	3545	0.0539	132.4	13.93
	3190	0.0594	115.2	14.37
Average	**3517**	**0.0576**	**124.9**	**15.1**
Std. Dev.	**291**	**0.0072**	**12.01**	**2.94**
X1-2672 neat/postcured 200	Yield Stress (psi)	Yield strain(in/in)	Modulus (ksi)	Toughness (inlb/in3
	4407	0.0503	154.9	15.36
	3559	0.0455	137	11.44
	3930	0.0461	152.5	12.76
	3981	0.0483	153.7	13.56
	4116	0.0511	160.9	15.31
	3855	0.0522	139.5	14.26
Average	**3975**	**0.0489**	**149.7**	**13.78**
Std. Dev.	**282**	**0.0027**	**9.398**	**1.53**
X1-2672/3% vinyl/postcured 200	Yield Stress (psi)	Yield stain(in/in)	Modulus (ksi)	Toughness (inlb/in3
	3246	0.0471	123.2	10.81
	3427	0.0519	121.1	12.61
	3827	0.063	127.6	17.63
	3106	0.0525	101.4	11.22
	3554	0.061	113	15.53
	3937	0.0734	117.8	21.34
Average	**3516**	**0.0582**	**117.4**	**14.86**
Std. Dev.	**324**	**0.0096**	**9.234**	**4.12**
X1-2672/6% vinyl/postcured 200	Yield Stress (psi)	Yield strain(in/in)	Modulus (ksi)	Toughness (inlb/in3
	2952	0.0476	112.4	9.993
	2920	0.0535	99.44	11.07
	2954	0.0572	105.6	12.53
	3293	0.0565	116.6	13.49
	3150	0.0526	110	11.73
	3025	0.0524	113.4	11.31
Average	**3049**	**0.0533**	**109.6**	**11.69**
Std. Dev.	**145**	**0.0034**	**6.178**	**1.214**
X1-2672/9% vinyl/postcured 200	Yield Stress (psi)	Yield strain(in/in)	Modulus (ksi)	Toughness (inlb/in3
	2632	0.0517	95.87	9.712
	2511	0.0515	89.76	9.13
	2633	0.0539	94.56	10.19
Average	**2592**	**0.0523**	**93.4**	**9.676**
Std. Dev.	**70**	**0.0013**	**3.216**	**0.529**

Figure B-1: Data from the flexural testing of X1-2672™ with vinyl terminated PDMS (DP_n=9) cured with the trifunctional cross-linker at 160°C/16 hours and post-cured at 200°C/4 hours.

X1-2672 neat/postcured 260	Yield Stress (psi)	Yield strain(in/in)	Modulus (ksi)	Toughness (inlb/in3)
	3670	0.032	170.1	7.887
	3725	0.0322	167.2	7.975
	3494	0.0331	136.7	7.525
	3691	0.0382	151.5	9.767
Average	**3645**	**0.0339**	**156.4**	**8.289**
Std. Dev.	**103**	**0.003**	**15.4**	**1.005**
X1-2672/3% vinyl/postcured 260	Yield Stress (psi)	Yield strain(in/in)	Modulus (ksi)	Toughness (inlb/in3)
	3687	0.0352	161	8.923
	3526	0.0428	142.8	10.55
	4075	0.0487	144.6	14.1
	3427	0.0445	120.7	10.57
Average	**3679**	**0.0428**	**142.3**	**11.04**
Std. Dev.	**285**	**0.0057**	**16.56**	**2.186**
X1-2672/6% vinyl/postcured 260	Yield Stress (psi)	Yield strain(in/in)	Modulus (ksi)	Toughness (inlb/in3)
	3334	0.0467	115.1	10.89
	3142	0.0414	121.9	8.99
	3455	0.0503	131.1	12.68
	3226	0.0492	114.3	11.29
	3265	0.0476	122.8	11.165
Average	**3284**	**0.047**	**121.1**	**11**
Std. Dev	**118**	**0.0034**	**4.354**	**1.323**
X1-2672/9% vinyl/postcured 260	Yield Stress (psi)	Yield strain(in/in)	Modulus (ksi)	Toughness (inlb/in3)
	2749	0.0491	104.3	9.669
	1997	0.028	89.3	3.638
	3012	0.0457	119.5	9.892
	2642	0.0366	116.5	6.711
Average	**2600**	**0.0399**	**107.4**	**7.477**
Std. Dev.	**431**	**0.0095**	**13.72**	**2.942**

Figure B-2: Data from the flexural testing of X1-2672™ with vinyl terminated PDMS ($DP_n=9$) cured with the trifunctional cross-linker at 160°C/16 hours and post-cured at 260°C / 8 hours .

2672nt/tetra/pstcd260	Yld. Strss(psi)	Yld. Strn(in/in)	Yngs Mod(ksi)	Tghns(inlb/in3)
	4199	0.0335	180	9.306
	3816	0.0282	191.1	7.198
	3964	0.0335	168.9	8.818
	3722	0.029	177.3	7.157
Average	3925	0.0311	179.3	8.12
Std. Dev.	208	0.0028	9.19	1.106
2672/3%Vi/tetra	Yld. Strss(psi)	Yld. Strn(in/in)	Yngs Mod(ksi)	Tghns(inlb/in3)
	4094	0.0456	146.9	12.83
	3259	0.0294	155.9	6.37
	2913	0.0234	160.8	4.318
	2901	0.0239	141.7	4.268
Average	3292	0.0306	151.3	6.947
Std. Dev.	560	0.0104	8.59	4.044
2672/6%Vi/tetra	Yld. Strss(psi)	Yld. Strn(in/in)	Yngs Mod(ksi)	Tghns(inlb/in3)
	2763	0.0265	140.7	4.765
	2771	0.0282	129.2	5.044
	1791	0.0168	117.1	1.794
	3058	0.0299	143.2	6.103
	2679	0.0242	143.6	4.079
Average	2612	0.0251	134.8	4.357
Std. Dev.	481	0.0051	11.49	1.607
2672/9%Vi/tetra	Yld. Strss(psi)	Yld. Strn(in/in)	Yngs Mod. (ksi)	Tghns(inlb/in3)
	114100	0.0345	114.1	6.214
	107300	0.0331	107.3	5.579
	109600	0.0302	109.6	4.685
	115100	0.0348	115.1	6.381
	109200	0.0391	109.2	7.37
	111200	0.04	111.2	7.857
Average	2676	0.0353	111.1	6.348
Std. Dev.	182	0.0037	3.021	1.157

Figure B-3: Data from the flexural testing of X1-2672™ with vinyl terminated PDMS (DP_n=9) cured with the tetrafunctional cross-linker at 140°C/16 hours and post-cured at 260°C/8 hours.

Sample	K1C(MPa.m.5)	G1C(N/m)	G1C(lb/in)
2672nt/nopostcure	0.36	151	0.859
	0.319	119	0.677
Average	**0.34**	**135**	**0.771**
2672nt/pstcrd200	0.303	89	0.506
	0.314	96	0.546
	0.325	102	0.582
	0.34	112	0.639
Average	**0.321**	**100**	**0.571**
3%vi/pstcrd200	0.32	126	0.72
	0.335	139	0.792
	0.318	125	0.713
	0.33	135	0.77
	0.348	150	0.856
	0.345	147	0.838
Average	**0.333**	**137**	**0.783**
6%vi/pstcrd200	0.343	156	0.888
	0.317	133	0.759
	0.325	139	0.796
Average	**0.328**	**143**	**0.817**
Sample	K1C(MPa.m.5)	G1C(N/m)	G1C(lb/in)
9%vi/pstcrd200	0.383	228	1.3
	0.272	115	0.658
	0.306	146	0.832
	0.262	107	0.61
	0.294	134	0.768
	0.285	127	0.723
Average	**0.3**	**143**	**0.817**

Figure B-4: Data from the fracture toughness testing of X1-2672™ with vinyl terminated PDMS (DP_n=9) cured with the trifunctional cross-linker at 260°C/16 hours and post-cured at 200°C / 4 hours.

Sample	K1C(MPa.m.5)	G1C(N/m)	G1C(lb/in)
2672nt/pstcrd260	0.261	63.2	0.36
	0.256	60.6	0.345
	0.314	91.4	0.52
	0.312	90.1	0.513
	0.338	106.3	0.605
Average	0.296	82	0.469
3%vi/pstcrd260	0.289	85	0.484
	0.32	104.3	0.593
	0.315	101.2	0.576
	0.346	121.7	0.692
Average	0.32	103	0.586
6%vi/pstcrd260	0.329	129.5	0.737
	0.342	140.2	0.798
	0.315	118.8	0.676
	0.312	116.9	0.665
	0.328	128.7	0.732
Average	0.325	127	0.722
9%vi/pstcrd260	0.38	195	1.11
	0.354	169.5	0.964
	0.364	179.3	1.02
	0.374	188.7	1.07
Average	0.368	183	1.04

Figure B-5: Data from the fracture toughness testing of X1-2672™ with vinyl terminated PDMS (DP_n=9) cured with the trifunctional cross-linker at 160°C/16 hours and post-cured at 260°C / 8 hours.

Sample	K1C(MPa.m.5)	G1C(N/m)	G1C(lb/in)
2672nt/tetra	0.265	56.8	0.324
	0.266	57.1	0.326
	0.327	86.6	0.495
Average	**0.286**	**66.8**	**0.381**
3% Vi/tetra	0.255	62.1	0.355
	0.272	70.7	0.404
	0.285	77.7	0.444
	0.207	40.9	0.234
	0.215	44.5	0.254
Average	**0.247**	**59.18**	**0.334**
6% Vi/tetra	0.281	84.9	0.485
	0.305	100.2	0.572
	0.282	85.4	0.488
	0.259	72	0.411
	0.417	187	1.07
	0.281	84.7	0.484
Average	**0.304**	**102.4**	**0.585**
9% Vi/tetra	0.285	105.7	0.604
	0.282	104.1	0.595
	0.373	182	1.04
	0.329	141.1	0.806
	0.356	165.2	0.943
	0.326	138.7	0.792
Average	**0.325**	**139.5**	**0.797**

Figure B-6: Data from the fracture toughness testing of X1-2672™ with vinyl terminated PDMS (DP_n=9) cured with the tetrafunctional cross-linker at 140°C/16 hours and post-cured at 260°C / 8 hours.

X1-2672 neat/postcured 200	Yield Stress (psi)	Yield strain (in/in)	Yng'sMod(ksi)	Tghns(inlb/in3)
	4407	0.0503	154.9	15.36
	3559	0.0455	137	11.44
	3930	0.0461	152.5	12.76
	3981	0.0483	153.7	13.56
	4116	0.0511	160.9	15.31
	3855	0.0522	139.5	14.26
Average	3975	0.0489	149.7	13.78
Std. Dev.	282	0.0027	9.398	1.53
X1-2672/3% silane/postcured 200	Yield Stress (psi)	Yield strain (in/in)	Yng'sMod(ksi)	Tghns(inlb/in3)
	4173	0.0535	155.9	16.31
	4072	0.0497	148.9	14.58
	3674	0.0341	168.8	8.56
Average	3973	0.0523	157.9	13.15
Std. Dev.	264	0.0013	10.05	4.065
X1-2672/6% silane/postcured 200	Yield Stress (psi)	Yield strain (in/in)	Yng'sMod(ksi)	Tghns(inlb/in3)
	3518	0.04	149.2	9.879
	3327	0.0295	158.9	6.537
	3424	0.0382	149.9	9.216
	3320	0.0378	132.4	8.483
Average	3397	0.0363	147.6	8.529
Std. Dev.	93	0.0046	11.06	1.445
X1-2672/9% silane/postcured 200	Yield Stress (psi)	Yield strain (in/in)	Yng'sMod(ksi)	Tghns(inlb/in3)
	3401	0.0462	132.8	11.37
	3904	0.0842	118.3	25.84
	3812	0.0898	116.1	27.32
	3329	0.0516	120.5	12.34
	3322	0.0621	113.2	15.38
	3207	0.0471	121	10.9
Average	3496	0.0635	120.3	17.19
Std. Dev.	289	0.0191	6.784	7.46

Figure B-7: Data from the flexural testing of X1-2672™ with silane terminated rubber (DP_n=4) cured with the trifunctional cross-linker at 160°C/16 hours and post-cured at 200°C/4 hours.

X1-2672neat/postcured260	Yield Stress (psi)	Yield strain (in/in)	Yngs Mod(ksi)	Tghns(inlb/in3)
	3670	0.032	170.1	7.887
	3725	0.0322	167.2	7.975
	3494	0.0331	136.7	7.525
	3691	0.0382	151.5	9.767
Average	3645	0.0339	156.4	8.289
Std. Dev.	103	0.003	15.4	1.005
X1-2672/3%silane/postcured260	Yield Stress (psi)	Yield strain (in/in)	Yngs Mod(ksi)	Tghns(inlb/in3)
	3731	0.0429	159.1	11.27
	3568	0.0411	154.3	10.25
	3704	0.0383	160.7	9.827
	3537	0.04	153.6	9.817
	3985	0.0491	147.7	14.06
Average	3705	0.0423	155.1	11.04
Std. Dev.	177	0.0042	5.11	1.785
X1-2672/6%silane/postcured260	Yield Stress (psi)	Yield strain (in/in)	Yngs Mod(ksi)	Tghns(inlb/in3)
	3593	0.0434	153.6	11.02
	3204	0.0387	132.9	8.547
	3246	0.0318	152.2	6.941
	3541	0.0417	127.1	10.31
	4172	0.0524	150.2	15.98
Average	3551	0.0416	105.9	10.56
Std. Dev.	388	0.0075	8.344	3.421
X1-2672/9%silane/postcured260	Yield Stress (psi)	Yield strain (in/in)	Yngs Mod(ksi)	Tghns(inlb/in3)
	2503	0.0349	104.3	5.973
	3307	0.0553	114.9	13.09
	3598	0.0531	132	13.85
	3384	0.0563	123.7	13.78
	3695	0.0614	124.5	16.29
Average	3297	0.0522	119.9	12.6
Std. Dev.	471	0.0101	10.63	3.895

Figure B-8: Data from the flexural testing of X1-2672™ with silane terminated rubber (DP_n=4) cured with the trifunctional cross-linker at 160°C/16 hours and post-cured at 260°C/8 hours .

X1-2672 neat/tetrafunctnl	Yield Stress (psi)	Yield strain (in/in)	Yngs Mod(ksi)	Tghns(inlb/in3)
	4199	0.0325	180	9.306
	3816	0.0282	191.1	7.198
	3964	0.0335	168.9	8.818
	3722	0.029	177.3	7.157
Average	**3925**	**0.0311**	**179.3**	**8.12**
Std. Dev	**208**	**0.0028**	**9.19**	**1.106**
X1-2672/3%silane/tetrafunctnl	Yield Stress (psi)	Yield strain (in/in)	Yngs Mod(ksi)	Tghns(inlb/in3)
	3159	0.0321	143.4	6.837
	3979	0.0404	157.5	10.82
	3300	0.0268	169.9	5.782
	3473	0.031	165.2	7.257
	3243	0.0274	159.4	5.829
Average	**3431**	**0.0315**	**159.1**	**7.305**
Std. Dev.	**327**	**0.0055**	**10.06**	**2.066**
X1-2672/6%silane/tetrafunctnl	Yield Stress (psi)	Yield strain (in/in)	Yngs Mod(ksi)	Tghns(inlb/in3)
	3017	0.0293	142.2	5.913
	3608	0.0351	157.4	8.564
	3014	0.0295	146.9	5.918
	3040	0.0294	152.8	5.888
	2938	0.0279	150.2	5.447
Average	**3123**	**0.0302**	**149.9**	**6.346**
Std. Dev.	**274**	**0.0028**	**5769**	**1.256**
X1-2672/9%silane/tetrafunctnl	Yield Stress (psi)	Yield strain (in/in)	Yngs Mod(ksi)	Tgns(inlb/in3)
	3103	0.0327	153.1	6.884
	3277	0.0432	129.9	9.875
	2997	0.0387	126.7	7.93
	2795	0.0309	134.9	5.907
	3220	0.0408	131.8	9.081
Average	**3078**	**0.0373**	**135.3**	**7.935**
Std. Dev.	**192**	**0.0053**	**10.39**	**1.604**

Figure B-9: Data from the flexural testing of X1-2672™ with silane terminated rubber (DP_n=4) cured with the tetrafunctional cross-linker at 140°C/16 hours and post-cured at 260°C / 8 hours .

Sample	K1C(MPa-m^1/2)	G1C(N/m)	G1C(lb/in)
X1-2672 neat/ pstcrd200	0.302	88.65	0.506
	0.314	95.61	0.546
	0.325	102.05	0.583
	0.340	111.94	0.639
Average	**0.321**	**99.60**	**0.568**
3%silane/pstcrd200	0.355	115.86	0.662
	0.386	137.13	0.783
	0.371	126.49	0.722
	0.395	143.28	0.818
Average	**0.377**	**130.70**	**0.746**
6%silane/pstcrd200	0.412	166.75	0.952
	0.383	144.36	0.824
	0.445	194.88	1.113
	0.412	167.09	0.954
	0.481	227.41	1.299
	0.383	144.28	0.824
Average	**0.419**	**174.20**	**0.994**
9%silane/pstcrd200	0.438	230.91	1.319
	0.401	194.33	1.110
	0.469	265.14	1.514
	0.452	245.81	1.404
Average	**0.440**	**234.00**	**1.340**

Figure B-10: Data from the fracture toughness testing of X1-2672™ with silane terminated rubber ($DP_n=4$) cured with the trifunctional cross-linker at 160°C/16 hours and post-cured at 200°C / 4 hours.

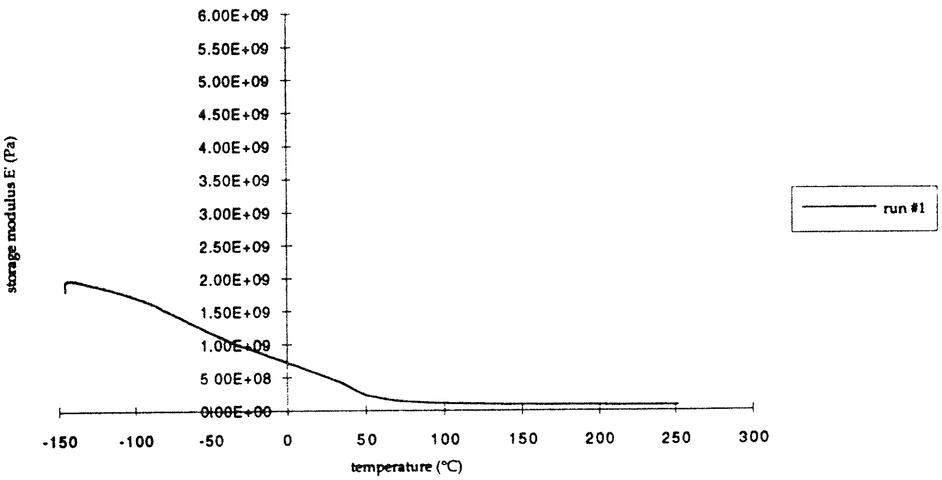
Sample	K1C(MPa-m^1/2)	G1C(N/m)	G1C(lb/in)
X1-2672 neat pstcrd260	0.261	63.20	0.361
	0.256	60.61	0.346
	0.314	91.36	0.522
	0.312	90.05	0.514
	0.338	106.25	0.607
Average	**0.296**	**82.30**	**0.470**
3%silane/pstcrd260	0.424	168.22	0.961
	0.368	126.40	0.722
	0.404	152.28	0.870
	0.394	145.00	0.828
Average	**0.397**	**148.00**	**0.845**
6%silane/pstcrd260	0.449	275.73	1.575
	0.406	225.64	1.289
	0.404	224.02	1.279
	0.411	231.57	1.323
Average	**0.418**	**239.20**	**1.370**
9%silane/pstcrd260	0.471	267.89	1.530
	0.473	270.78	1.546
	0.526	334.29	1.909
	0.446	241.02	1.376
	0.478	276.77	1.581
	0.496	297.34	1.698
Average	**0.482**	**281.40**	**1.61**

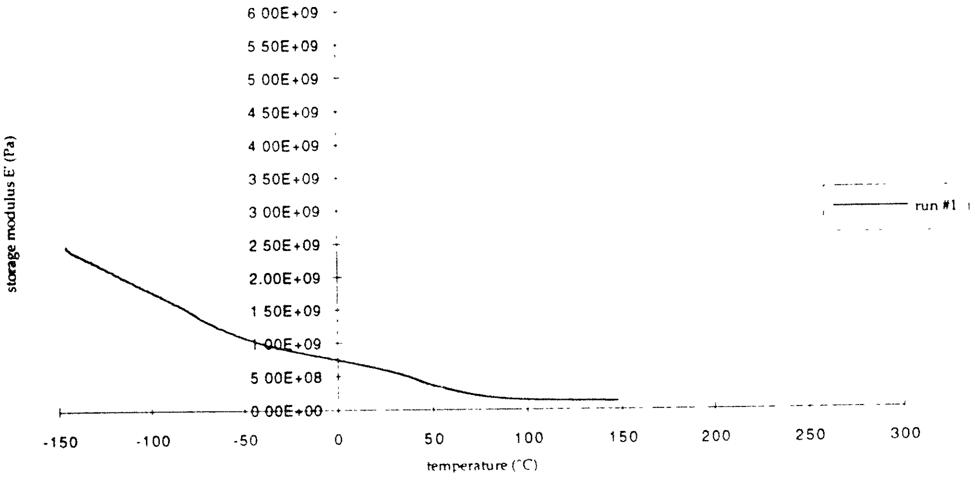
Figure B-11: Data from the fracture toughness testing of X1-2672™ with silane terminated rubber (DPn=4) cured with the trifunctional cross-linker at 160°C/16 hours and post-cured at 260°C/8 hours.

Sample	K1C(MPa-m^1/2)	G1C(N/m)	G1C(lb/in)
X1-2672neat/tetrafunctnl	0.265	56.80	0.324
	0.266	57.10	0.326
	0.327	86.60	0.495
Average	**0.286**	**66.80**	**0.281**
3%silane/tetrafunctnl	0.301	82.71	0.472
	0.309	87.08	0.497
	0.286	74.63	0.426
	0.251	57.40	0.328
	0.220	44.28	0.253
	0.419	160.10	0.914
Average	**0.297**	**84.36**	**0.482**
6%silane/tetrafunctnl	0.357	123.00	0.702
	0.341	112.51	0.643
	0.313	94.52	0.540
	0.421	171.28	0.978
	0.300	87.16	0.498
	0.321	99.62	0.569
Average	**0.342**	**114.70**	**0.655**
9%silane/tetrafunctnl	0.375	150.75	0.861
	0.410	180.18	1.029
	0.443	210.02	1.199
	0.386	160.09	0.914
	0.348	129.80	0.741
Average	**0.393**	**166.20**	**0.949**

Figure B-12: Data from the fracture toughness testing of X1-2672™ with silane terminated rubber (DPn=4) cured with the tetrafunctional cross-linker at 140°C/16 hours and post-cured at 260°C/8 hours.

Appendix C


Storage modulus E' X1-2672 with 12% vinyl terminated PDMS cured with trifunctional cross-linker.


Storage modulus E' of X1-2672 with 6% vinyl terminated PDMS cured with trifunctional cross-linker.

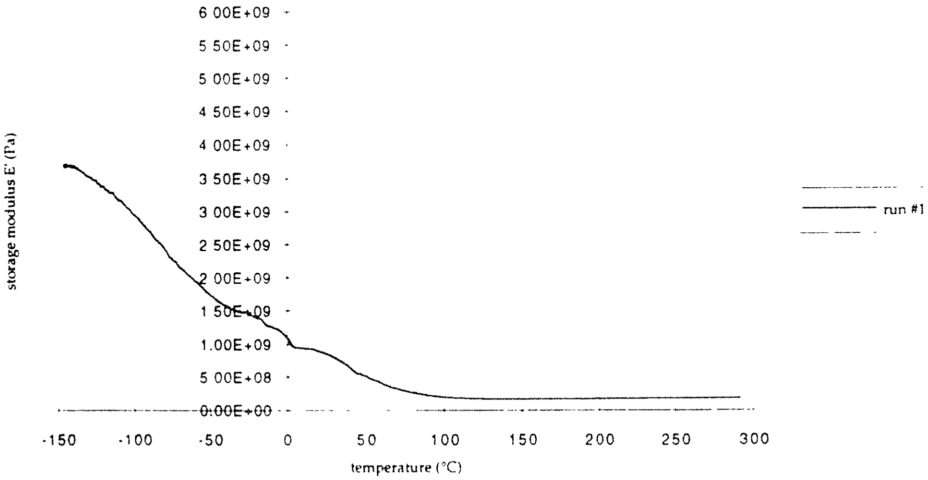
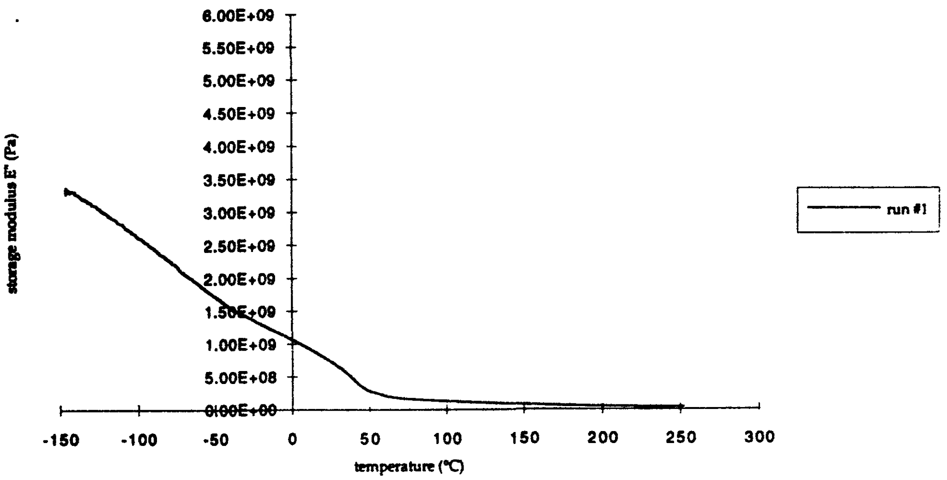
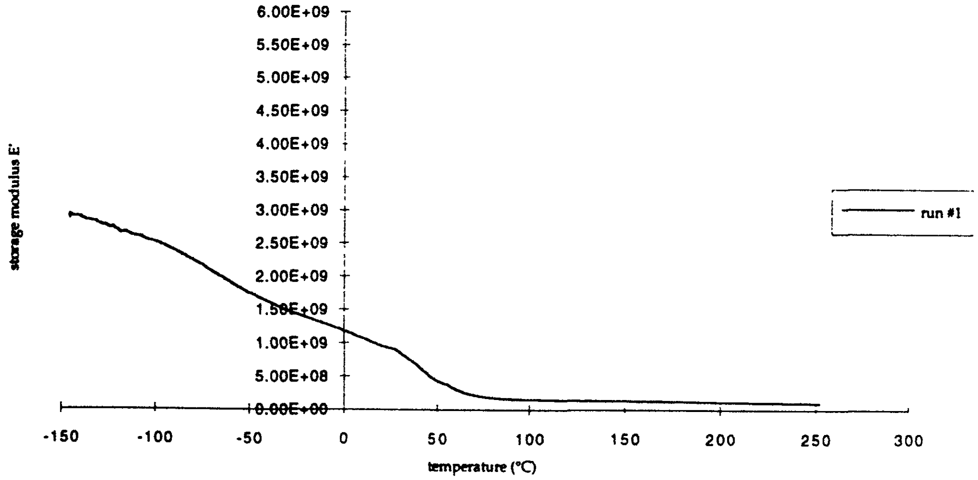

Storage modulus E' of X1-2672 neat resin cured with trifunctional cross-linker.

Figure C-1: Storage modulus variation with temperature, at a rate of 2°C/min and a frequency of 5 Hz, for X1-2672™ resin with 0,6, and 12% vinyl terminated PDMS (DP_n=9), cured with the trifunctional cross-linker at 160°C/16 hours and post-cured at 260°C/8 hours

Storage Modulus E' of X1-2672 with 12% silane terminated rubber cured with trifunctional cross-linker.



Storage modulus E' of X1-2672 with 6% silane terminated rubber cured with trifunctional cross-linker.



Storage modulus E' of X1-2672 neat resin cured with trifunctional cross-linker.

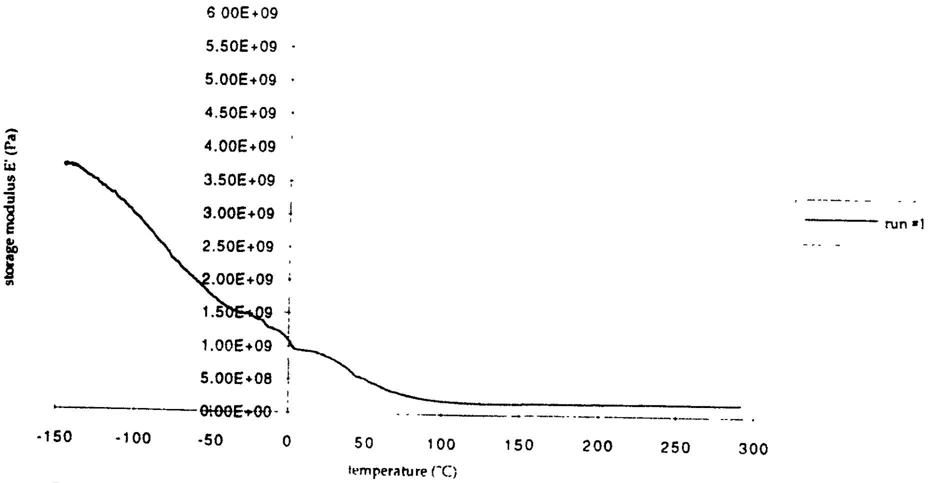
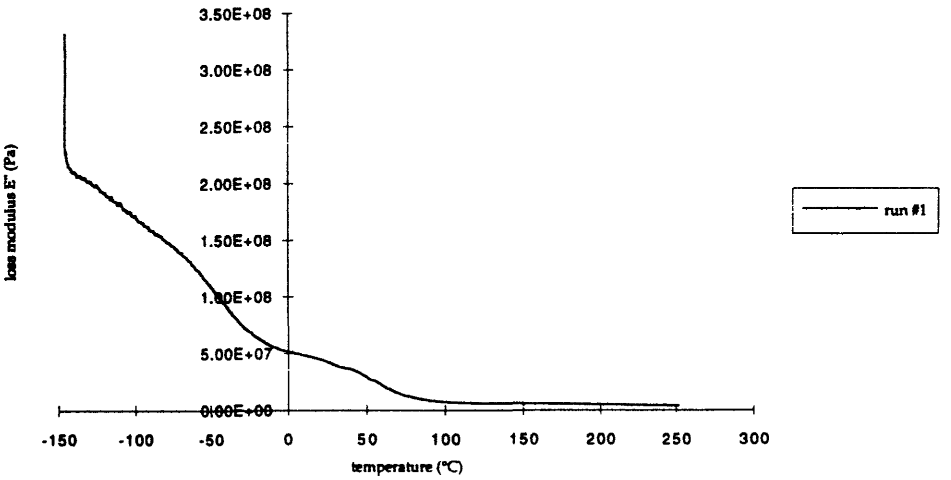
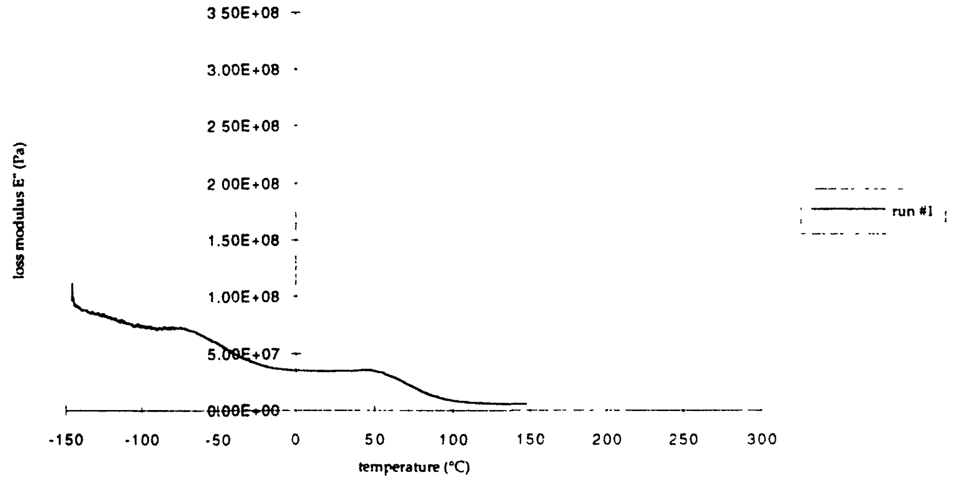


Figure C-2: Storage modulus variation with temperature, at a rate of 2°C/min and a frequency of 5 Hz, for X1-2672™ resin with 0,6, and 12% silane terminated rubber (DP_n=4), cured with the trifunctional cross-linker at 160°C/16 hours and post-cured at 260°C/8 hours

Loss modulus E" of X1-2672 with 12% vinyl terminated PDMS cured with trifunctional cross-linker.



Loss modulus E" of X1-2672 with 6% vinyl terminated PDMS cured with trifunctional cross-linker.



Loss Modulus E" of X1-2672 resin cured with trifunctional cross-linker.

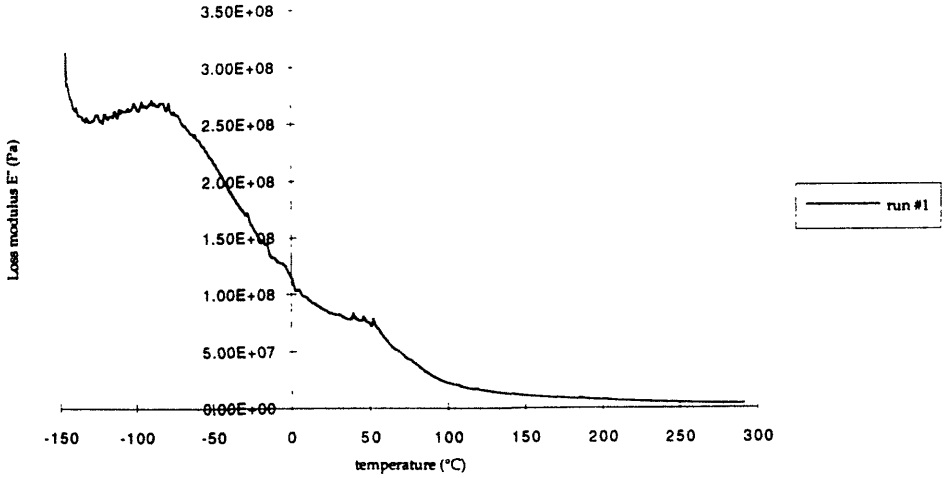
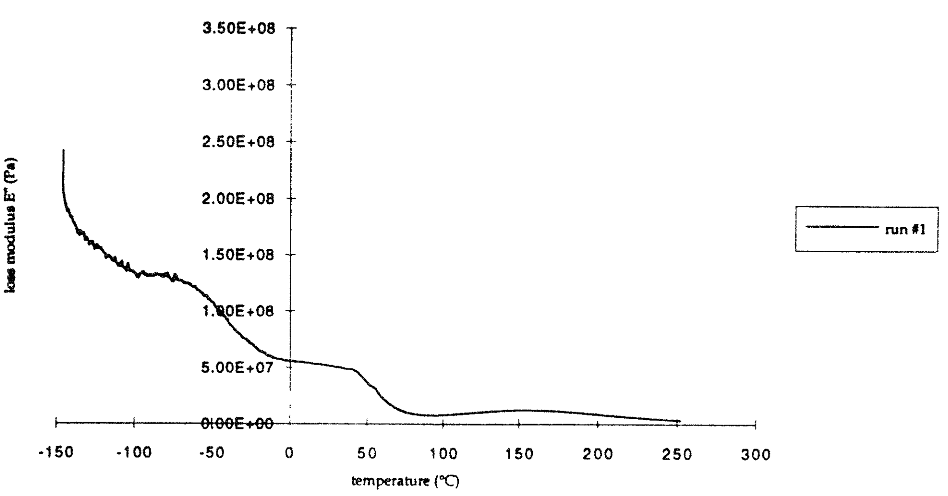
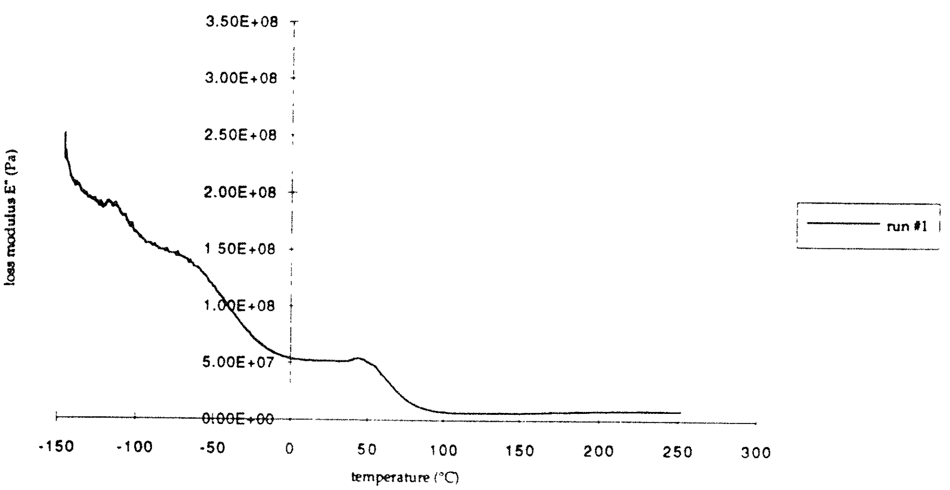


Figure C-3: Loss modulus variation with temperature, at a rate of 2°C/min and a frequency of 5 Hz, for X1-2672™ resin with 0,6, and 12% vinyl terminated PDMS (DP_n=9), cured with the trifunctional cross-linker at 160°C/16 hours and post-cured at 260°C/8 hours.

Loss modulus E" of X1-2672 with 12% silane terminated rubber cured with trifunctional cross-linker.



Loss Modulus E" of X1-2672 with 6% silane terminated rubber cured with trifunctional cross-linker.



Loss Modulus E" of X1-2672 resin cured with trifunctional cross-linker.

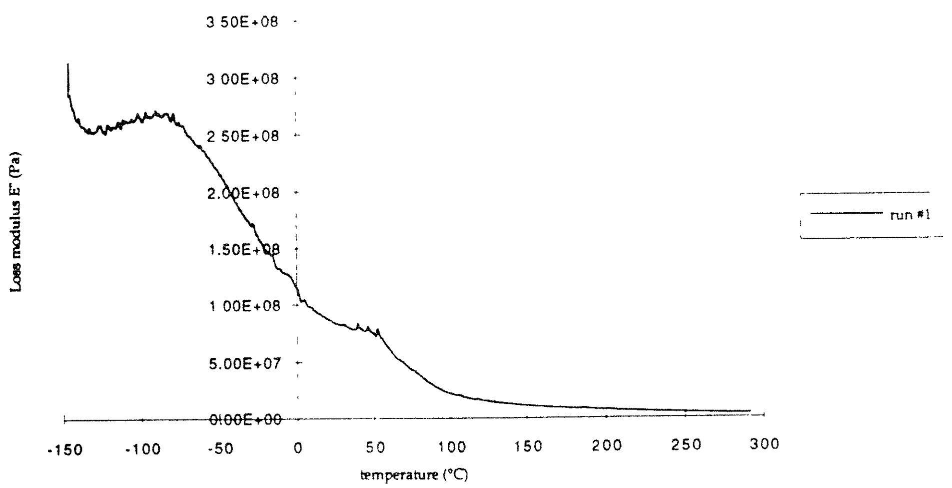


Figure C-4: Loss modulus variation with temperature, at a rate of 2°C/min and a frequency of 5 Hz, for X1-2672™ resin with 0,6, and 12% silane terminated rubber (DP_n=4), cured with the trifunctional cross-linker at 160°C/16 hours and post-cured at 260°C/8 hours.

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