Chapter 4

Evaluation of adhesive performance

PART 1

4.1 ADHESIVE BONDING OF DIFFERENT SUBSTRATES

4.1.1 INTRODUCTION

4.1.2 EXPERIMENTAL
   a. Materials
   b. Preparation of PCF resin
   c. Metal-metal bonding
   d. Rubber-rubber bonding

4.1.3 RESULTS AND DISCUSSION

4.1.4 CONCLUSION

PART 2

4.2 AGEING STUDIES ON ADHESIVE BONDS

4.2.1 INTRODUCTION

4.2.2 EXPERIMENTAL
   a. Metal-metal bonding
   b. Rubber-rubber bonding
   c. Rubber-metal bonding
   d. Ageing studies
   e. Storage life of the adhesive

4.2.3 RESULTS AND DISCUSSION
   a. Ageing under ambient conditions
   b. Ageing in hot air oven
   c. Ageing in hot water
   d. Ageing in salt water
e. Ageing of CR/ENR based adhesives
f. Storage life of the adhesive

4.2.4 CONCLUSION

REFERENCES
4.1 ADHESIVE BONDING OF DIFFERENT SUBSTRATES

4.1.1 INTRODUCTION

Advantages of adhesive bonding include the ability to join dissimilar materials, the ability to join thin sheets efficiently and increase in design flexibility. Of the many adhesive types, structural adhesives are extensively used in the aerospace industry to join metals such as aluminium, titanium and their respective alloys. These adhesives are often based on low molar-mass phenolic or epoxy resins, which polymerise or cure to give highly crosslinked adhesives. Cardanol based resins are desirable starting materials for adhesive formulations due to their renewable nature, high polarity and inherent tackiness.

All metals have a relatively high surface energy and are generally considered easy to bond. A base metal is highly reactive in most cases and forms various oxides, sulphides and hydrates when exposed to the atmosphere. Hence during metal-to-metal bonding, it is important to consider not only the bulk metal but also the ability to bond to its hydrated oxide. In the case of aluminium, the oxide is extremely stable and serves as a protective coating. Aluminium is an ideal substrate for adhesives. It has high energy and is very resistant to most environments [1]. It is also a material with good formability and high strength to weight ratio. Hence, adhesive-bonded aluminium joints are commonly used in the aircraft and automotive industries.

The use of organic structural adhesives for the industrial production of steel joints is first referred to in the paper by Preiswerk and Zeerleder [2]. After the introduction of phenolic resins for adhesive-bonded aluminium joints de Bruyne and others [3, 4] pointed out the usefulness of epoxide resins as structural adhesives for practically all technical materials, including steel. It was further realised that steel joints could also be produced by using adhesives based on phenolic, polyester and acrylic resins. Titanium is widely used in aerospace
applications that require high strength-to-weight ratio at elevated temperatures [1]. It also shows good fracture toughness and creep resistance.

In the case of elastomeric substrates two different types of bonding are possible. In one type, already vulcanized elastomers are bonded using adhesives. This is termed as 'post-vulcanized bonding'. In the second type an adhesive bond is created during the vulcanization of the elastomer. This is termed as 'vulcanized bonding'. When bonding to post-vulcanized elastomers, one is working with an elastomeric substrate that is completely cured and formed [1, 5].

In this part of the work, the effectiveness of a blend of neoprene and phenol-cardanol-formaldehyde (PCF) resin adhesive system for bonding the following substrates is investigated. a) Aluminium (Al), stainless steel (SS), titanium (Ti) and galvanized iron (GI) as metal substrates and b) SBR (Styrene butadiene rubber), NR (Natural rubber), NBR (Acrylonitrile butadiene rubber), CR (chloroprene rubber) and EPDM (ethylene propylene diene monomer) as elastomer substrates. The metal substrates selected are three common materials employed for structural applications. The elastomers are five most common rubbers employed in industries. The optimum resin content that gives the maximum bond strength in each case is also identified.

4.1.2. EXPERIMENTAL

a. Materials

The chloroprene (neoprene) rubbers AD and W were obtained from DuPont, Akron, Ohio. Styrene butadiene rubber (SBR 1502) was obtained from Japan Synthetic Rubber Co. Ltd., Tokyo. ISNR-5 (Indian Standard Natural Rubber) was supplied by the Rubber Research Institute of India, Kottayam, India. Acrylonitrile butadiene rubber (N 553 with 33% acrylonitrile content) was obtained from Apar Polymers Ltd, Mumbai, India. EPDM was supplied by DuPont, USA. CNSL (Cashew nut shell liquid) was procured from Vijayalakshmi Cashew Exports, Kollam, India. Carbon black (HAF) was obtained from Phillips Carbon Black Ltd., Cochin, India and it had the following specifications- Dibutylphthalate (DBP)
adsorption - 102± 5ml/ 100g and iodine number- 82. Precipitated silica used in this study was GSL-150 grade procured from Sameera Chemicals, Kottayam, India. 3-Aminopropyltriethoxysilane was obtained from Sigma Aldrich, Bangalore, India.

The aluminium substrate used in this study was extruded aluminium alloy AA 6060-T6 and had a thickness of 1.6mm. It was supplied by Hindalco Industries Ltd, Mumbai, India. The composition of this alloy by weight is 0.46% Mg, 0.4% Si, 0.18% Fe, 0.021% Mn, 0.002% Cu, 0.015% Zn, 0.01% Ti and rest Al. Stainless steel used was of the type A403 and grade WP304 of thickness 1mm. It has a composition of 0.08% (max) C, 2% Mn, 0.045% (max) P, 0.03% (max) S, 1% Si, 18-20% Cr, 8-11% Ni and rest Fe. It was supplied by Tata Iron and Steel Company Ltd., Jamshedpur, India. Titanium alloy used was Ti-6Al-4V of 1mm thickness. Galvanized iron used was of general purpose and had a thickness of 1.8mm.

b. Preparation of copolymer (PCF) resin

PCF resin was synthesized by reacting a mixture of phenol and cardanol with formaldehyde at 90-95°C for about one hour. The resins were prepared with a stoichiometric ratio of 1:1.7 between total phenols and formaldehyde in an alkaline medium. The resole type resin obtained was neutralized using oxalic acid and dried. Two different phenolic resins with varying phenol / cardanol ratio (wt%), viz. 60 / 40 (PCF-I) and 80 / 20 (PCF-II), were synthesized.

c. Metal to metal bonding

i. Substrate preparation

Metal strips of size 100x 25 mm were machined from plain sheets to serve as metal substrates for lap shear strength studies on metal-to-metal bonds. Mechanical cleaning (surface roughening) was done with a No. 100 emery paper. Solvent degreasing with trichloroethylene followed mechanical cleaning.

ii. Adhesive preparation

Neoprene rubber for the adhesive formulation was masticated on a two-roll mill along with other ingredients and was dissolved in toluene so as to obtain a 15 wt%
solution. The PCF resin was dissolved in methyl ethyl ketone separately and subsequently blended with the rubber solution. The formulations are given in Table 4.1.1 For metal-to-metal bonding only PCF-II was used in the adhesive system because earlier studies [Section 2.3.2.f] has proved the effectiveness of this resin for this purpose. The resin (PCF-II) concentration was varied from 40 to 100phr in steps of 20phr. A set of experiments was also carried out using the basic adhesive formulation, i.e. without the resin.

Table 4.1.1 Adhesive formulation

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Al-to-Al bonding (Formulation-1)</th>
<th>SBR-to-SBR bonding (Formulation-2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neoprene AD</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Neoprene W</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Silica</td>
<td>4phr</td>
<td>-</td>
</tr>
<tr>
<td>Acetylene black</td>
<td>-</td>
<td>6phr</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1phr</td>
<td>0.5phr</td>
</tr>
<tr>
<td>Zinc phosphate</td>
<td>1.5phr</td>
<td>-</td>
</tr>
<tr>
<td>Silane</td>
<td>2phr</td>
<td>-</td>
</tr>
<tr>
<td>PCF resin</td>
<td>40-100 phr</td>
<td>0-50 phr</td>
</tr>
<tr>
<td>Solid content wt%</td>
<td>15-17</td>
<td>20-22</td>
</tr>
</tbody>
</table>

After applying the adhesive, the substrates were kept aside for half an hour to evaporate the solvent. The adhesive was applied to a thickness of 0.1mm. It was applied on both substrates. The substrates were then subsequently bonded together and the adhesive cured for 30 minutes at 150°C by employing a pressure of 12.5 kg/cm².
d. Rubber to rubber bonding

i. Substrate preparation

1. SBR substrate

SBR is a copolymer of styrene (i.e. vinyl benzene) and butadiene. It is considered as a general purpose rubber as it can be used for many applications and especially in tyre compounds. With the exception of some grades, the styrene content is 23.5% by wt. Based on the polymerisation reaction temperature it is classified into cold SBR (4°C) or hot SBR (50°C) grades. The 1500 series is a cold polymerised non-pigmented type rubber. The structure of SBR can be represented as

\[
\begin{align*}
\text{CH}_2 & - \text{CH} = \text{CH} - \text{CH}_2 \underbrace{\text{CH}_2}_{x} \underbrace{\text{CH}}_{y} \\
\end{align*}
\]

Table 4.1.2 SBR substrate compounding recipe

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR 1502</td>
<td>100</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1</td>
</tr>
<tr>
<td>HAF</td>
<td>50</td>
</tr>
<tr>
<td>Aromatic oil</td>
<td>10</td>
</tr>
<tr>
<td>Vulcanox HS</td>
<td>1</td>
</tr>
<tr>
<td>Vulcanox 4020</td>
<td>1</td>
</tr>
<tr>
<td>MBTS</td>
<td>0.5</td>
</tr>
<tr>
<td>TMTD</td>
<td>0.5</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1</td>
</tr>
</tbody>
</table>
The rubber compounding for the preparation of elastomeric substrates was done on a laboratory size (15 x 30 cm) two-roll mill at a friction ratio of 1:1.25 as per ASTM D3186. It was done as mentioned in Section 2.2.1.b. The compounding recipe for SBR substrate is given in Table 4.1.2. Typical cure curve obtained is shown in Fig. 4.1.1. A cure time of 11.9 minutes is obtained. Optimum cure time is the time required for a torque value of \[ (T_{\text{max}} - T_{\text{min}}) \times 0.9 + T_{\text{min}} \], where \( T_{\text{max}} \) is the maximum torque and \( T_{\text{min}} \) is the minimum torque.

![Cure graph of SBR substrate](image)

**Fig. 4.1.1 Cure graph of SBR substrate**

2. **CR substrate**

Chloroprene rubbers are manufactured by polymerising 2-chloro-1,3-butadiene in the presence of catalysts, emulsifying agents, modifiers and protective agents. The polymer chain is built up through addition of monomer units, of which approximately 98% add in the 1,4positions. Pure gum vulcanizates of CR show high levels of tensile strength. They show high resistance to oxidative ageing and flex cracking CR has inherent flame resistance because of the presence of chlorine molecule and products made from it are normally self extinguishing. The structure of CR is represented as

\[
\begin{align*}
\text{Cl} \\
\text{CH}_2 \quad \text{C} \quad \text{CH} \quad \text{CH}_2 \\
\end{align*}
\]
Table 4.1.3 CR substrate compounding recipe

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR-W</td>
<td>100</td>
</tr>
<tr>
<td>ZnO</td>
<td>4</td>
</tr>
<tr>
<td>MgO</td>
<td>5</td>
</tr>
<tr>
<td>HAF</td>
<td>40</td>
</tr>
<tr>
<td>Aromatic oil</td>
<td>6</td>
</tr>
<tr>
<td>NA22</td>
<td>0.5</td>
</tr>
</tbody>
</table>

During compounding, CR is first masticated on a two roll mill. To protect against scorching, MgO is added first followed by HAF and aromatic oil. ZnO and NA 22 are added last. It is then homogenized and sheeted out and kept 22 hours for maturation. After maturation the cure time is determined. The compounding formulation is given in Table 4.1.3. The cure curve is shown in Fig. 4.1.2. A typical marching curve is obtained. The cure time is obtained as 20.5 minutes.

![Cure graph of CR substrate](image)

**Fig. 4.1.2 Cure graph of CR substrate**

3. **NBR substrate**

Nitrile rubbers are manufactured by emulsion copolymerisation of butadiene rubber with acrylonitrile. It is characterized by excellent oil resistance, solvent
resistance and fuel resistance. The physical properties of nitrile rubbers are good when the rubbers are compounded with carbon black. It possesses better heat resistance than CR but prone to ozone cracking. The structure can be represented as

\[
\begin{align*}
\text{CH}_2 - & \text{CH}=\text{CH} - \text{CH}_2 \mid_x \text{CH}_2 - \text{CH} \mid_y \\
\text{CN}
\end{align*}
\]

The compounding of NBR is similar that of SBR. But as sulphur is less soluble in nitrile rubber, it is added first to get a good dispersion. This is followed by the other ingredients in the following order: ZnO, stearic acid, HAF, DOP, antioxidants and accelerators. The compounding recipe is given in Table 4.1.4. After homogenization it is sheeted out and matured. Later the cure time is determined. The cure time is 5.1 minutes. The curve graph is given in Fig 4.1.3.

Table 4.1.4 NBR substrate compounding recipe

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
</tr>
<tr>
<td>HAF</td>
<td>45</td>
</tr>
<tr>
<td>DOP</td>
<td>10</td>
</tr>
<tr>
<td>Vulcanox 4020</td>
<td>1.5</td>
</tr>
<tr>
<td>MBTS</td>
<td>1</td>
</tr>
<tr>
<td>TMTD</td>
<td>0.5</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1.5</td>
</tr>
</tbody>
</table>
NR substrate

NR is the most widely used elastomer. The rubber hydrocarbon component of NR consists of over 99.9% of linear cis-1,4-polyisoprene. The raw NR has good strength and building tack. It also shows excellent extrudability and calenderability. The structure of NR is represented as

\[
\begin{align*}
\text{CH}_3 \\
\text{CH}_2 - \text{C} \quad \text{CH} \quad \text{CH}_2 \quad \text{n}
\end{align*}
\]

NR was compounded in the same way as SBR. The compounding recipe is given in Table 4.1.5. The cure curve is shown in Fig. 4.1.4. The cure graph shows a reversion after 15 minutes. The cure time obtained is 6.61 minutes.
Table 4.1.5 NR substrate compounding recipe

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>100</td>
</tr>
<tr>
<td>ZnO</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
</tr>
<tr>
<td>HAF</td>
<td>40</td>
</tr>
<tr>
<td>Aromatic oil</td>
<td>3</td>
</tr>
<tr>
<td>Vulcanox HS</td>
<td>1</td>
</tr>
<tr>
<td>Vulcanox 4020</td>
<td>0.5</td>
</tr>
<tr>
<td>CBS</td>
<td>0.6</td>
</tr>
<tr>
<td>TMTD</td>
<td>0.3</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2</td>
</tr>
</tbody>
</table>

Fig. 4.1.4 Cure graph of NR substrate

5. **EPDM substrate**

The monomers ethylene and propylene are copolymerised with Zeigler-Natta type catalysts. The properties of the copolymers depend on the relative proportion of the two monomer units in the chain, the average molecular weight, the molecular distribution and the relative content of propylene in the head and tail positions. In addition to these olefins, the EPDM contains a non-conjugated diene as the third monomer. The third monomer in the EPDM used was dicyclopentadiene (DCPD).
The structure can be represented as shown below. EPDM vulcanizates show excellent resistance to oxygen and ozone.

![Chemical Structure](image)

Table 4.1.6 EPDM substrate compounding recipe

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM</td>
<td>100</td>
</tr>
<tr>
<td>ZnO</td>
<td>4</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1.5</td>
</tr>
<tr>
<td>HAF</td>
<td>50</td>
</tr>
<tr>
<td>Paraffinic oil</td>
<td>10</td>
</tr>
<tr>
<td>Vulcanox 4020</td>
<td>1</td>
</tr>
<tr>
<td>MBTS</td>
<td>1</td>
</tr>
<tr>
<td>TMTD</td>
<td>0.5</td>
</tr>
<tr>
<td>ZDC</td>
<td>0.5</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1</td>
</tr>
</tbody>
</table>

Fig 4.1.5 Cure graph of EPDM substrate
The compounding formulation of EPDM substrates is given Table 4.1.6. The typical cure curve obtained is given in Fig. 4.1.5. The cure time is found to be 10.22 minutes.

ii. Adhesive preparation

A 20wt% solution of neoprene rubber in toluene along with other ingredients – carbon black and sulphur (Table 4.1.1) was prepared. Only PCF-I was used in the blend in view of earlier observations [Section 2.3.2.f] regarding the suitability of this resin for rubber-to-rubber bonding. The total resin (PCF-I) concentration in the adhesive was varied from 0 to 50phr in steps of 10phr.

The adhesive solution was applied to an approximate thickness of 0.1mm on both rubber substrates. After drying for about 30 minutes, the substrates were joined and curing was done at 150°C for 30 minutes applying a pressure of 12.5kg/cm².

4.1.3 RESULTS AND DISCUSSION

![Graph](image)

**Figure 4.1.6 Effect of varying resin content on shear strength in metal-metal bonding**

Fig. 4.1.6 shows the effect of varying the resin content on metal-to-metal shear strength. In most cases the shear strength value increases with resin content. As the resin content increases, the modulus of the adhesive increases. Furthermore, phenolic resin molecules have many OH groups and hence show good affinity towards metal surfaces [6], and this results in strong metal-metal bonds. The effect of resin addition is not very noticeable in the case of GI-GI. In the case of GI, the
outermost film of zinc or its oxide may be involved in chemical interaction with the neoprene rubber in the adhesive. Zinc oxide is the crosslinking agent for neoprene rubber (Table 4.1.3). This may explain the lack of improvement in lap shear strength on addition of resin in this case. In the case of aluminium and titanium the maximum shear strength is observed on addition of 80phr resin. In the case of SS-SS bonding, the shear strength increases with resin content and reaches a maximum at 100phr resin. This can be attributed to the higher modulus of steel. It is reported that chromium based adhesion promoters are used as primers to increase the strength and durability of adhesive joints [7]. Hence the presence of chromium in stainless steel might have contributed to the higher bond strength of SS-SS joints.

![Figure 4.1.7 Effect of varying resin content on peel strength in rubber-rubber bonding](image)

Figure 4.1.7 Effect of varying resin content on peel strength in rubber-rubber bonding

Fig 4.1.7 shows the variation of peel strength with resin content in rubber-to-rubber bonding. In this case also the peel strength increases with resin content initially, reaches a maximum and then decreases. The maximum peel strength was obtained at 10phr resin. As the resin content increases the flexibility of the adhesive film decreases, which leads to inferior peel strength values. It was also found that SBR-SBR bonds gave the highest peel strength. SBR has a lower Young’s modulus compared to other rubbers. It is possible that the mismatch of moduli is the least in the case of SBR and the adhesive.
Fig 4.1.8 shows the effect of resin content on shear strength of rubber-to-rubber bonds. Though the highest shear strength was obtained with SBR-SBR specimens, bond failure with fracture of the substrates occurred in all the cases. It was found that in the case of SBR and NBR the shear strength value increases with resin content up to 30phr and then decreases. This may be due to their similarity in reactivity and unsaturation arising from the diene structure. CR has a high level of crystallinity and NR shows stress-induced crystallization. Addition of resin beyond a certain level may hinder the tendency to crystallization and hence the incorporation of more resin leads a detrimental effect on shear strength.

![Graph showing effect of varying resin content on shear strength in rubber-rubber bonding](image)

**Figure 4.1.8 Effect of varying resin content on shear strength in rubber-rubber bonding**

Though theoretically possible, EPDM rubbers cannot be cured by resin in practical use [8]. Hence the addition of higher amount of resin for bonding EPDM substrates will not have a positive effect in the absence of a chemical interaction. Among the different elastomers, SBR shows the highest bondability and EPDM the lowest. This can be attributed to the highest and lowest bondability index values of SBR and EPDM, respectively [1]. The polar-nonpolar incompatibility may also lead to the inferior bond strengths in the case of EPDM and NR. Table 4.1.7 shows some mechanical properties of the rubber substrates used for bonding.
### Table 4.1.7 Mechanical properties of rubber vulcanizates

<table>
<thead>
<tr>
<th>Elastomer</th>
<th>SBR</th>
<th>CR</th>
<th>NBR</th>
<th>NR</th>
<th>EPDM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>15</td>
<td>15.2</td>
<td>18.6</td>
<td>20.6</td>
<td>23.3</td>
</tr>
<tr>
<td>Modulus (MPa)</td>
<td>4.01</td>
<td>4.01</td>
<td>5.97</td>
<td>7.55</td>
<td>5.47</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>793</td>
<td>793</td>
<td>735</td>
<td>633</td>
<td>895</td>
</tr>
<tr>
<td>Hardness (Shore A)</td>
<td>60</td>
<td>60</td>
<td>65</td>
<td>62</td>
<td>68</td>
</tr>
</tbody>
</table>

### 4.1.4 CONCLUSION

A copolymer of phenol-cardanol-formaldehyde along with neoprene rubber constitutes an effective adhesive system for bonding different rubber-to-rubber, metal-to-metal and rubber-to-metal combinations. In the case of metal-to-metal bonding, SS-SS shows the highest shear strength values of the order of 12MPa. For rubber-to-rubber bonding, SBR-SBR bonds yield the best peel and shear strength values.

### PART 2

#### 4.2 AGEING STUDIES ON ADHESIVE BONDS

#### 4.2.1 INTRODUCTION

For an adhesive to be useful, it should not only withstand the mechanical forces that are acting on it, but must also resist the elements to which it is exposed during service. Thus, one of the most important characteristics of an adhesive joint is its endurance to the operating environment. This endurance is also known as joint permanence or durability. The permanence of the adhesive joints depends on environmental elements like high and low temperatures, moisture or relative humidity, chemical fluids and outdoor weathering.

All polymeric materials are degraded to some extent by exposure to elevated temperatures. To withstand elevated temperature exposure, an adhesive must have high melting or softening point and resistance to oxidation. Exposure to high
temperatures results in chain scission leading to decreased molecular weight of the
bulk polymer. This results in both reduced cohesive strength and brittleness. Many
of the base resins used in high temperature adhesive formulations are rigidly
crosslinked or are made -up of a molecular backbone referred to as a ‘ladder
structure’. The ladder structure provides high bond dissociation energy and acts as
an energy sink to its environment [1]. The rigidity of the molecular chain decreases
the possibility of chain scission by preventing thermally agitated vibration of the
chemical bonds.

Water is the substance that causes the greatest problems to the environmental
stability of adhesive joints. Water may enter and alter a joint by one or a
combination of the following processes [9]. It may enter the joint by diffusion
through the adhesive, by transport along the interface, by capillary action through
cracks and crazes in the adhesive or by diffusion through the adherend if it is
permeable. The water admittes can alter the properties of the adhesive in a
reversible (plasticization of the adhesive) or in an irreversible (causing hydrolysis,
cracking or crazing) manner. It can also attack the adhesive/adherend interface
either by displacing the adhesive or by hydrating the metal or metal oxide surface
of the adherend.

For most bonded metal joints, corrosive environments are a more serious
problem than the influence of moisture. Of the different corrosive environments,
salt can have a severe effect on joint strength durability. It was found that exposure
to a 5% salt spray for three months had a more severe effect on aluminium joints
than exposure to a semi-tropical environment for three years [10]. On exposure to
sea water, corrosion of the metal interface occurs resulting in a weak boundary
layer.

In this section, the results of ageing studies conducted on Al-Al, Al-SBR and
SBR- SBR bonds are presented. The adhesive employed was an optimal
composition developed during studies reported in Chapters 2 & 3. The ageing
process was mostly done in a heated air oven at 100°C for 24 hours. In addition,
ageing in different environments like hot water and salt water is also investigated.
4.2.2 EXPERIMENTAL

a. Metal to metal bonding

Aluminium substrates for both peel and shear studies were prepared by mechanical cleaning followed by solvent degreasing. The following cases were studied.

i. Neoprene based formulation containing 80phr phenol cardanol formaldehyde (PCF) resin. For peel studies a 60/40 P/C resin and for shear studies a 80/20 P/C resin of 1:1.7 stoichiometric ratio between total phenols and formaldehyde were used.

ii. Neoprene based formulation containing the optimum blend of PCF and EPN resins (40 & 60 parts respectively), keeping the total resin content at 80phr.

iii. Neoprene based formulation containing a commercially available phenolic resin viz. para-tertiary butyl phenolic resin (PTBP).

iv. Neoprene based formulation containing a blend of PTBP and EPN resins (40 & 60 parts respectively) keeping the total resin content at 80phr.

Table 4.2.1 The formulation of adhesive used for Al-Al bonding

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Al-to-Al bonding (Formulation 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neoprene AD</td>
<td>90</td>
</tr>
<tr>
<td>Neoprene W</td>
<td>10</td>
</tr>
<tr>
<td>Silica</td>
<td>4phr</td>
</tr>
<tr>
<td>Acetylene black</td>
<td>-</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1phr</td>
</tr>
<tr>
<td>Zinc phosphate</td>
<td>1.5phr</td>
</tr>
<tr>
<td>Silane</td>
<td>2phr</td>
</tr>
<tr>
<td>i. PCF resin</td>
<td>80phr</td>
</tr>
<tr>
<td>ii. PCF/EPN resin</td>
<td>40/60 by wt</td>
</tr>
<tr>
<td>iii. PTBP resin</td>
<td>80phr</td>
</tr>
<tr>
<td>iv. PTBP/EPN resin</td>
<td>40/60 by wt</td>
</tr>
<tr>
<td>Solid content %</td>
<td>15-17</td>
</tr>
</tbody>
</table>
For the next part of the study an adhesive formulation containing Neoprene AD (70 parts by wt.) and epoxidized natural rubber (ENR) (30 parts by wt.) along with 80phr PCF / PTBP resin was used. Only peel strength of Al-Al bonds was evaluated under different ageing conditions.

b. Rubber to rubber bonding

SBR substrates of dimension 100 x 25 x 2 mm were prepared to serve as rubber substrates. The following systems were studied:

i. Neoprene based formulation containing 20phr phenol cardanol formaldehyde (PCF) resin. For peel studies and shear studies a 60/40 P/C resin of 1:1.7 stoichiometric ratio between total phenols and formaldehyde was employed.

ii. Neoprene based formulation containing the optimum blend of PCF and EPN resins (70 /30 parts respectively), keeping the total resin content at 20phr.

iii. Neoprene based formulation containing a commercially available phenolic resin viz. para-tertiary butyl phenolic resin (PTBP).

iv. Neoprene based formulation containing a blend of PTBP and EPN resins (70 /30 parts respectively), keeping the total resin content at 20phr.

For the second part of the study, an adhesive formulation containing Neoprene W (80 parts by wt) and ENR (20 parts by wt) along with 20phr PCF/PTBP resin was used. Only peel strength of SBR-SBR was evaluated under different ageing conditions.
Table 4.2.2 Formulation of adhesive used for SBR-SBR bonding

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>SBR-to-SBR bonding (Formulation 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neoprene AD</td>
<td>90</td>
</tr>
<tr>
<td>Neoprene W</td>
<td>10</td>
</tr>
<tr>
<td>Silica</td>
<td>-</td>
</tr>
<tr>
<td>Acetylene black</td>
<td>6phr</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.5phr</td>
</tr>
<tr>
<td>Zinc phosphate</td>
<td>-</td>
</tr>
<tr>
<td>Silane</td>
<td>-</td>
</tr>
<tr>
<td>i. PCF resin</td>
<td>20phr</td>
</tr>
<tr>
<td>ii. PCF/EPN resin</td>
<td>80/20 by wt</td>
</tr>
<tr>
<td>iii. PTBP resin</td>
<td>20phr</td>
</tr>
<tr>
<td>iv. PTBP/EPN resin</td>
<td>80/20 by wt</td>
</tr>
<tr>
<td>Solid content %</td>
<td>20-22</td>
</tr>
</tbody>
</table>

c. Rubber to metal bonding

In rubber to metal bonding, SBR served as the metal substrate and aluminium as the metal substrate. A primer-adhesive combination was used for the bonding. The adhesive formulated earlier for Al-Al bonding served as the primer for SBR-Al bonding and the formulation for SBR-SBR bonding served as the adhesive. Both peel and shear studies were carried out on rubber-metal joints.

d. Ageing studies

The following ageing studies were conducted on the specimens.

i. Ageing under ambient conditions for 3 months. The samples were tested after 3 months exposure to outside atmosphere

ii. Air-oven ageing at 100°C for 24 hours

iii. Hot water ageing by immersing the samples in boiling water for 24 hours
iv. Salt water ageing by immersing the samples in collected sea water for 3 months. The samples were periodically tested.

e. Storage life of the adhesive

The test is based on ASTM D 1337. The adhesives selected for this study were a) the optimum SBR-SBR formulation and b) the primer or the optimised formulation for Al-Al bonding. These consisted of neoprene and PCF blends developed in Chapter 2. Samples were bonded using the same adhesive after passage of definite intervals of time and tested. Peel tests were performed for metal-metal, rubber-rubber and rubber-metal joints. The total period of time covered was 19-20 days.

4.2.3 RESULTS AND DISCUSSION

a. Ageing under ambient conditions

![Graph showing peel strength comparison](image)

Fig 4.2.1 SBR-SBR peel specimens bonded using different adhesives and aged under ambient conditions
Fig 4.2.2 SBR-SBR shear specimens bonded using different adhesives and aged under ambient conditions

Fig 4.2.3 Al-Al peel specimens bonded using different adhesives and aged under ambient conditions

Fig 4.2.4 Al-Al shear specimens bonded using different adhesives and aged under ambient conditions
Fig 4.2.5 SBR-AI peel specimens bonded using different adhesives and aged under ambient conditions

![Peel strength comparison graph]

Fig 4.2.6 SBR-AI shear specimens bonded using different adhesives and aged under ambient conditions

![Shear strength comparison graph]

Table 4.2.3 Properties after ageing under ambient conditions for 3 months

<table>
<thead>
<tr>
<th>Ageing condition</th>
<th>Resin system used</th>
<th>SBR- SBR</th>
<th>Al - Al</th>
<th>SBR- Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>% fall in peel strength</td>
<td>% fall in shear strength</td>
<td>% fall in peel strength</td>
</tr>
<tr>
<td>Ambient conditions - 3 months</td>
<td>PCF</td>
<td>1.02</td>
<td>Shear strength not affected</td>
<td>3.90</td>
</tr>
<tr>
<td></td>
<td>PCF + EPN</td>
<td>2.2</td>
<td></td>
<td>1.88</td>
</tr>
<tr>
<td></td>
<td>TBP</td>
<td>2.15</td>
<td></td>
<td>5.00</td>
</tr>
<tr>
<td></td>
<td>TBP + EPN</td>
<td>5.38</td>
<td></td>
<td>1.58</td>
</tr>
</tbody>
</table>

174
Figs 4.2.1-4.2.6 and Table 4.2.3 show the loss in adhesive property of SBR-SBR, Al-Al and SBR-Al bonds when aged under ambient conditions i.e. at relative humidity of 85% and at room temperature for 3 months. It can be seen that in rubber-rubber bonding, the PCF based system shows the highest strength retention after ageing, though the highest bond strengths are obtained for those systems containing EPNs. From the figures it can be concluded that the bond strength of the adhesive joints does not deteriorate when aged under ambient conditions.

b. Ageing in hot air oven

![Peel strength](image)

Fig 4.2.7 SBR-SBR peel specimens bonded using different adhesives and oven aged at 100°C

![Shear strength](image)

Fig 4.2.8 SBR-SBR shear specimens bonded using different adhesives and oven aged at 100°C
Fig 4.2.9 Al-Al peel specimens bonded using different adhesives and oven aged at 100°C

Fig 4.2.10 Al-Al shear specimens bonded using different adhesives and oven aged at 100°C

Fig 4.2.11 SBR-Al peel specimens bonded using different adhesives and oven aged at 100°C
Figs 4.2.7 – 4.2.12 and Table 4.2.4 show the behaviour of SBR-SBR, Al-Al and SBR-Al bonds on exposure to hot air at 100°C. In the case of SBR-SBR peel strength, there is a drastic reduction in magnitude for the resin system containing PCF and EPN resins. The presence of higher functionality in EPN resins results in a higher degree of crosslinking. During ageing at elevated temperature, additional crosslinks may occur resulting in a highly crosslinked network. This may also result in modulus mismatch between the adhesive film and the substrate in rubber-rubber bonding leading to adhesive failure at low loads.
c. Ageing in hot water

Fig 4.2.13 SBR-SBR peel specimens bonded using different adhesives and aged at 100°C water

Fig 4.2.14 SBR-SBR shear specimens bonded using different adhesives and aged at 100°C water

Fig 4.2.15 Al-Al peel specimens bonded using different adhesives and aged at 100°C water
Fig 4.2.16 Al-Al shear specimens bonded using different adhesives and aged at 100°C water

Fig 4.2.17 SBR-Al shear peel specimens bonded using different adhesives and aged at 100°C water

Fig 4.2.18 SBR-Al shear specimens bonded using different adhesives and aged at 100°C water
Table 4.2.3 Properties after ageing in hot water for 24 hours

<table>
<thead>
<tr>
<th>Ageing condition</th>
<th>Resin used</th>
<th>SBR -SBR</th>
<th>Al - Al</th>
<th>SBR - Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot water-100°C for 24 hours</td>
<td>PCF</td>
<td>14.4</td>
<td>Shear strength not affected</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PCF + EPN</td>
<td>31.2</td>
<td>10.32</td>
<td>20.3</td>
</tr>
<tr>
<td></td>
<td>TBP</td>
<td>14.9</td>
<td>15.6</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>TBP + EPN</td>
<td>22.9</td>
<td>14.2</td>
<td>15.9</td>
</tr>
</tbody>
</table>

Figs. 4.2.13 - 4.2.18 and Table 4.2.5 show the effect of SBR-SBR, Al-Al and SBR-Al bonds on exposure to hot water at 100°C for 24 hours. It can be seen that fall in adhesive properties is slightly higher on exposure to hot water. Water is the substance that gives the greatest problems in terms of environmental stability for many adhesive joints. Water is a problem because it is very polar and permeates most polymers. Moisture may enter by wicking along the adhesive-adherend interface or by wicking along the interfaces caused by reinforcing fibres and the resin. The presence of moisture can degrade the adhesive properties at the interface. The temperature may also enhance the degradation.

d. Ageing in salt water

![Graph](image)

**Fig 4.2.19** SBR-SBR peel specimens bonded using different adhesives and aged in salt water
Fig 4.2.20 Al-Al peel specimens bonded using different adhesives and aged in salt water

Fig 4.2.21 Al-Al shear specimens bonded using different adhesives and aged in salt water

Fig 4.2.22 SBR-Al peel specimens bonded using different adhesives and aged in salt water
Table 4.2.6 Properties after ageing in salt water for 3 months

<table>
<thead>
<tr>
<th>Ageing condition</th>
<th>Resin system used</th>
<th>SBR-SBR</th>
<th>Al-Al</th>
<th>SBR-Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>% fall in peel strength</td>
<td>% fall in peel strength</td>
<td>% fall in shear strength</td>
</tr>
<tr>
<td>Salt water for 3 months</td>
<td>PCF</td>
<td>11.6</td>
<td>34.6</td>
<td>24.8</td>
</tr>
<tr>
<td></td>
<td>PCF + EPN</td>
<td>13.9</td>
<td>33.1</td>
<td>24.2</td>
</tr>
<tr>
<td></td>
<td>TBP</td>
<td>24.0</td>
<td>31.7</td>
<td>43.5</td>
</tr>
</tbody>
</table>

Figs. 4.2.19 - 4.2.23 and Table 4.2.6 show the effect of salt water ageing on SBR-SBR, Al-Al and SBR-Al bonds. The presence of salt can have a very severe effect on joint strength durability. Deterioration in joint strength is normally much more rapid with salt solution than with water. This supports the view that corrosive attack along the bondline is involved in the presence of salt whereas attack by water first involves diffusion through the adhesive [11].
e. Ageing of CR/ENR based adhesives

Fig 4.2.24 SBR-SBR peel specimens bonded using CR/ENR based adhesives and aged under ambient condition, hot air and hot water

Fig 4.2.25 Al-Al peel specimens bonded using CR/ENR based adhesives and aged under ambient condition, hot air and hot water

Fig 4.2.26 SBR-Al peel specimens bonded using CR/ENR based adhesives and aged under ambient condition, hot air and hot water
Fig 4.2.27 SBR-SBR shear specimens bonded using CR/ENR based adhesives and aged under ambient conditions, hot air and hot water

Table 4.2.7 Properties after ageing for adhesives with and without ENR

<table>
<thead>
<tr>
<th>Elastomer and resin used</th>
<th>Ageing details</th>
<th>SBR- SBR</th>
<th>Al- Al</th>
<th>SBR- Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>% fall in peel strength</td>
<td>% fall in peel strength</td>
<td>% fall in peel strength</td>
</tr>
<tr>
<td>CR &amp; PCF</td>
<td>Ambient – 3 months</td>
<td>1.0</td>
<td>3.9</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>Hot air 70°C</td>
<td>13.4</td>
<td>8.0</td>
<td>12.3</td>
</tr>
<tr>
<td></td>
<td>Hot water 70°C</td>
<td>14.4</td>
<td>10.3</td>
<td>16.2</td>
</tr>
<tr>
<td>CR + ENR &amp; PCF</td>
<td>Ambient – 3 months</td>
<td>1.1</td>
<td>2.5</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Hot air 70°C</td>
<td>19.6</td>
<td>17.8</td>
<td>9.9</td>
</tr>
<tr>
<td></td>
<td>Hot water 70°C</td>
<td>21.0</td>
<td>21.0</td>
<td>12.8</td>
</tr>
<tr>
<td>CR &amp; TBP</td>
<td>Ambient – 3 months</td>
<td>2.1</td>
<td>5.0</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>Hot air 70°C</td>
<td>13.5</td>
<td>8.3</td>
<td>30.8</td>
</tr>
<tr>
<td></td>
<td>Hot water 70°C</td>
<td>14.9</td>
<td>19.0</td>
<td>37.1</td>
</tr>
<tr>
<td>CR + ENR &amp; TBP</td>
<td>Ambient – 3 months</td>
<td>7.2</td>
<td>5.10</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>Hot air 70°C</td>
<td>20.6</td>
<td>18.5</td>
<td>25.3</td>
</tr>
<tr>
<td></td>
<td>Hot water 70°C</td>
<td>21.6</td>
<td>22.3</td>
<td>30.5</td>
</tr>
</tbody>
</table>
Figs. 4.2.24-4.2.27 and Table 4.2.7 show the ageing properties on using CR-AD and ENR as elastomers. From the figures and table it can be seen that drastic reduction in adhesive strength occurs when exposed to hot water at 100°C. The water entering an adhesive joint may alter the properties of the adhesives in a reversible manner: i.e. they may produce plasticization effect on the bonded area. The temperature may enhance the diffusion phenomenon. It is reported that silanes used as adhesion promoters form polysiloxane coatings on the metal surface [12]. Though they may lead to more durable interfaces, they also greatly assist the entry of water into adhesive joints. It is also noted that the addition of ENR improves the ageing properties to a small extent.

**f. Storage life of the adhesive**

![Graph showing variation of peel strength with time](image)

Fig 4.2.28 Variation of peel strength with time

Fig. 4.2.28 shows the dependence of peel strength of the adhesive joints on the storage life of the adhesive. From the graph we can see that the peel strength of SBR-SBR bonds is unaltered with time. This shows that the adhesive used for joining rubber-rubber substrates is stable over a period of time. But in the case of SBR-Al bonds the mode of failure changes from cohesive to a mixed mode and later to adhesive after a week. This may be due to the hydrolysis and polymerization reactions of the silane with the phenolic resins and moisture.
4.2.4 CONCLUSION

From the ageing studies performed, it is found that the bonded specimens do not lose adhesive strength when aged under ambient conditions. But when the specimens are exposed to elevated temperatures they are showing a reduction of adhesive properties. This effect is enhanced when the samples are kept in water at 100°C. The addition of EPN and ENR improves the initial joint strength. Specimens bonded with formulations containing EPN are showing slightly higher resistance when aged in salt water. From the storage life studies it is found that the formulation developed for rubber-rubber bonding is quite stable while the formulation developed for metal-metal bonding is losing adhesive strength with time. From the ageing studies it is amply proved that the cardanol based resins has clear superiority over the commercially available para tertiary butyl phenolic resin.
REFERENCES