CHAPTER VII
SUMMARY AND CONCLUSION

The first chapter gives an introduction about oils and fats. Their general structure and specifications like SV, IV etc are explained. The major industrial uses of oils and fats are discussed in detail. The effect of the fatty acid composition of the oil and the alkali used, on the nature of the soaps is briefly discussed. The classification of oils based on unsaturation and the use of oils in paints and varnishes are briefly discussed. The film drying mechanism of oils are discussed in detail. The production of various chemicals derived from oils is summarised. A detailed survey of the use of vegetable oils in the field of polymers is given in this chapter. Majority of the references cited shows its use as plasticizers. So a discussion about the theories of plasticization, along with a survey of different types of materials used as plasticizer like, petroleum oil, pine products, esters and vegetable oils, is attempted. As the present work is on the use of vegetable oils, like linseed, soyabean, castor, rubber seed and punnal oil, in elastomers a detailed survey of their earlier uses is made. The survey also includes the use of derivatives of the oils in the field of plastics and rubbers. The anticipated suitability of these oils as multipurpose additive in elastomers is established by evaluating their V.G.C. and other properties like free fatty acid content and non-glyceride components. The principal objectives of the present study are pointed out briefly.

Chapter II gives the specifications of all the materials used in the study and summarises the different experimental techniques used in the study. The flow behaviour of the compounds were studied using Brabender plasticorder, the cure characteristics were studied using Elastograph, and the physical properties of the vulcanizates were studied using Universal
Testing Machine. The abrasion resistance of the vulcanizates were studied using a DIN abrader as per DIN standard. The compression set of the vulcanizates was determined as per ASTM D 395. The rebound resilience test was carried out as per ASTM D-2632. The ageing resistance was studied as per ASTM 573-88. The chemical crosslink density was determined by equilibrium swelling methods. The heat build up of the vulcanizates was studied using Goodrich flexometer.

Chapter III gives a general introduction about nitrile rubber. NBR is classified into three categories based on the ACN content. The properties of the elastomer depends on the ACN content. The general behaviour of the elastomer during compounding and curing is discussed. NBR is compounded basically like natural rubber. But as the solubility of sulphur is lower in NBR sulphur is added first during compounding. The cure rate of NBR is also fast. Since NBR is polar, usually esters like DOP or DOS are used as plasticizers. A detailed study of the use of linseed oil, soyabean oil, castor oil, rubber seed oil and punnal oil in nitrile rubber compounding is given in this chapter. These oils are used in place of DOP and stearic acid and the properties of the compound and vulcanizates are evaluated. Linseed oil marginally lowers the viscosity of the compound along with higher cure rate compared to DOP. The tensile strength, modulus, and tear resistance of the vulcanizates are improved by the substitution of DOP with linseed oil. It also decreases the leachability and reduces blooming, by maintaining, the air and oil resistance of the vulcanizates. 2-5 phr linseed oil is found to be an optimum concentration that can substitute 6 phr DOP and 2 phr stearic acid in NBR vulcanizates.

Substitution of DOP with soyabean oil also is seen to be advantageous. The processability of the compound is increased, and cure time is reduced. The cure rate is proportional to the oil concentration. The tensile strength, modulus and tear resistance are
increased, along with reduced compression set, blooming and leachability. The oil resistance is improved, while air resistance is unaffected. 4 phr soyabean oil is found to be the optimum concentration which can substitute 6 phr DOP and 2 phr stearic acid in nitrile rubber vulcanizates.

Substitution of DOP with castor oil increases the viscosity of the mix. The theoretical aspects relating to this is discussed. The cure time is increased. But castor oil gives appreciable increase in tensile strength, tear resistance, and ageing resistance with reduced leachability to the vulcanizates. 5-6 phr castor oil is the optimum concentration, which gives advantages in properties, if lower processability can be ignored.

Rubber seed oil, gave a comparable viscosity and cure characteristics to NBR with that of DOP. Tensile strength, tear resistance and modulus of the vulcanizates are increased, along with ageing resistance leachability and blooming are reduced, but compression set is slightly increased. 4-6 phr rubber seed oil is found to be the optimum concentration, that can substitute 6 phr aromatic oil and 2 phr stearic acid in NBR. Punnal oil is also found to be a good substitute for DOP in NBR vulcanizates. The oil gives advantage in processability, cure time, with improvements in physical properties like tensile strength, tear resistance, modulus and compression set. It also reduces leachability and blooming. The optimum concentration of punnal oil is found to be 3-5 phr that can advantageously substitute 6 phr aromatic oil and 2 phr stearic acid in NBR vulcanizates.

Chapter IV deals with a detailed study of the effect of vegetable oils on the cure characteristics and vulcanize properties of SBR. A brief discussion about the elastomer and the compounding methods adopted, are summarised in this chapter. Linseed oil is tried as a
substitute for aromatic oil and stearic acid. It marginally increases the viscosity and cure time of the compounds. Though an improvement in ageing resistance resilience and De Mattia flex resistance are observed, it marginally affects tensile strength, tear resistance, abrasion resistance and compression set. Properties like heat build up, modulus and elongation are unaffected. Linseed oil cannot be considered as a potential additive for SBR particularly as a replacement for aromatic oil. Substitution of aromatic oil with soyabean oil marginally affects the processability. It improves the vulcanizate properties like ageing resistance, De Mattia flex resistance and abrasion resistance. The tensile properties and compression set are unaffected. The cure rate also is unaffected 6-8 phr soyabean oil can substitute 6 phr aromatic oil and 2 phr stearic acid in SBR vulcanizates with the benefit of avoiding aromatic oil and balancing the advantages and disadvantages in properties of compounds and vulcanizates. Castor oil is not a good additive for SBR. Though improvement is seen in cure time and De Mattia flex resistance, all other properties are adversely affected or unaffected. Rubber seed oil is found to be an advantageous substitute for aromatic oil in SBR. It gives appreciable increase in properties like tensile strength, tear resistance De Mattia flex resistance, and rebound resilience to SBR vulcanizates. The compression set of the vulcanizates is reduced while cure rate and ageing resistance are increased. The optimum concentration of rubber seed oil is found to be 5-6 phr that can advantageously substitute 6 phr aromatic oil and 2 phr stearic acid in SBR vulcanizates. Punnal oil imparts improvement in properties like, tensile strength, tear resistance and abrasion resistances, De Mattia flex resistance and resilience to SBR vulcanizates. Processability of the compound is unaffected, while cure rate is increased. 5-6 phr punnal oil is found to be the optimum concentration. Chapter V deals with the effect of vegetable oils on the cure characteristics and vulcanizate properties of natural rubber. Linseed oil is a very good multipurpose additive in natural rubber. The processability is increased and cure time is decreased. The tensile strength, tear resistance, abrasion resistance, and heat build
up are unaffected other vulcanizes properties like ageing resistance, compression set, De Mattia flex resistance and resilience are improved. 2-4 phr linseed oil is an optimum concentration, which can advantageously substitute 6 phr aromatic oil and 2 phr stearic acid in natural rubber vulcanizates. Substitution of aromatic oil with soyabean oil reduces the viscosity of NR compounds with increased cure rate. The oil improves the vulcanizate properties like ageing resistance, abrasion resistance resilience and De Mattia flex resistance, while tensile strength, tear resistance and heat build up are unaffected. 2-4 phr soyabean oil is found to be the optimum concentration. Castor oil is seen to be most plasticizing in NR compared to other oils. Along with high reduction in viscosity, the cure time also is reduced. The theoretical aspects of this phenomenon are discussed later. Though no much improvement is seen in tensile strength tear resistance and abrasion resistance, advantages is seen in properties like De Mattia flex resistance, compression set, resilience and heat build up. Th optimum concentration is seen to be 2-3 phr. Rubber Seed oil is a good substitute for aromatic oil in natural rubber vulcanizates. Though there is a slight disadvantage in processability, cure time is considerably reduced. The tensile strength, tear resistance abrasion resistance, De Mattia flex resistance ageing resistance and resilience of the vulcanizates are improved, whereas heat build up and compression set are unaffected. The optimum concentration is found to be 6-8 phr that can substitute 6 phr aromatic oil and 2 phr stearic acid in NR vulcanizates. Punnal oil is also found to be a good substitute for aromatic oil in natural rubber. Though it marginally increases the viscosity, cure time is marginally reduced. The tensile strength, tear resistance ageing resistance, and resilience of the vulcanizates are increased without affecting the compression set, abrasion resistance and heat build up. 6-8 phr is the optimum concentration, that can substitute 6 phr aromatic oil and 2-phr stearic acid.
Chapter VI deals with the effect of vegetable oils on the properties of some typical rubber products. Substitution of aromatic oil with vegetable oils show mixed effect on the viscosities of the compounds. Castor oil marginally lowered the viscosity while rubber seed oil and punnal oil marginally increased the viscosity. Linseed and soyabean oil do not affect the viscosity. The cure time of the compounds are lowered by all the oils tried.

Tensile strength of tread is marginally increased by linseed oil soyabean oil and castor oil, whereas it is considerably increased by rubber seed oil and punnal oil. Tear resistance also showed a similar variation. De Mattia flex resistance is considerably increased and ageing resistance is marginally improved by all the oils. All the oils moderately improve the resilience. The heat build up of the vulcanizates are not affected by the oils. Linseed oil is found to be a good substitute for paraffinic oil in microcellular soles. It considerably increases the flex resistance without affecting the abrasion resistance. Punnal oil also can be used in M.C soles as it does not affect any of the properties. But soyabean oil, castor oil and rubber seed oil are found to decrease the flex resistance of the soles. All the vegetable oils tried are found to be good substitutes for aromatic oil in natural rubber sponge. They improve the compression deflection, without affecting the compression set and ageing resistance.

The summary of the effect of all these oils on the cure characteristics and vulcanizate properties of NBR, SBR, and NR are given in the following chart.
### Summary of the Advantages and Disadvantages in Properties by Use of Vegetable Oils

<table>
<thead>
<tr>
<th>Property</th>
<th>NR</th>
<th>BR</th>
<th>NBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Processability</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Cure time</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tear Resistance</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Modulus</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Elongation at Break</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Heat Build up</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Air Ageing Resistance</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Oil Ageing Resistance</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Leachability</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
| Advantage        | Moderate Advantage |               | Moderate Advantage |}

**Legend:**
- : Advantage
- : Moderate Advantage
- : Slight Disadvantage
- : Disadvantage
- : Moderate Disadvantage
- : Advantage
Structure dependence of plasticizer action and effect on cure rate

A major outcome of the present study is the establishment of the relation between processability and cure rate, and the relation of both with the structure of the elastomer and the plasticizer. It is generally known that the viscosity of any material is lowered where intermolecular force is reduced. Processability of any elastomer is achieved by reducing the viscosity, for which processing aids or plasticizers are used. Along with the major theories of plasticization viz. 1. The solvation theory 2. Lubricity theory 3. Gel theory and 4. Free volume theory. It is also mentioned that viscosity is reduced when intermolecular attraction between the polymer is reduced. The different intermolecular interaction in a compound are the Elastomer-Elastomer (EE interaction), the plasticizer-plasticizer (PP interaction) and the Elastomer Plasticizer interaction (EP interaction). Any plasticizer is considered to be good, when the EE interaction and the EP interaction are lower than the original EE interaction or PP interactions. The usual interactive forces between molecules are the Van der Waals' force, the London force and the hydrogen bond. Hydrogen bond is the strongest among them. A material can highly affect the viscosity if it can produce or break hydrogen bonds. Use of castor oil as ingredient in Nitrile rubber, highly increases the viscosity of the compounds. This is due to the strong hydrogen bond formed between cyano nitrogen of the elastomer and the hydroxyl hydrogen of the plasticizer. The same castor oil highly reduces the viscosity of natural rubber. This is because of the repulsive force between Elastomer and plasticizer which in turn reduces the EE interaction. This theory is against the solvation theory, according to which, a plasticizer is compatible with the polymer, when they are of same nature (like dissolves like). But the conclusion that a good plasticizer may not be a good solvent or may not be compatible with the elastomer is supported by the above observations.
Plasticizer effect on cure rate

The same observation correlates the plasticizing ability to cure rate. The rate of any reaction depends on the activation energy of the molecules taking part. A plasticizer due to its structure can activate or deactivate a polymer molecule. When the plasticizer, which is non compatible with the polymer enters into the polymer, the polymer-polymer interaction is reduced, and the molecule become activated, and the cure rate will be faster, as in the case of castor oil in NR. The action of castor oil in NBR is in the opposite direction. It forms strong hydrogen bond with adjacent elastomer molecule, reducing the energy of the reacting molecule, and the cure rate is lowered.

So it is concluded that a plasticizer, which increases the polymer-polymer interaction or polymer-plasticizer interaction, is a poor plasticizer, and it will reduce the cure rate. On the other hand a chemically non compatible plasticizer will reduce the intermolecular forces of attraction, between the elastomer molecules, activating it, which results in highly reduced viscosity and increases cure rate.