CHAPTER 5

PREPARATION AND PROPERTIES OF SILICONE ELASTOMERS

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1. Introduction

Silicones have been commercially available since the 1940's and the most dominant member of this class of synthetic polymers is poly(dimethylsiloxane), (PDMS) -[(CH$_2$)$_2$SiO]$_n$-. The polysiloxane or silicone industry may be conveniently grouped into products based upon fluids (which may or may not contain functional groups), cross-linked elastomers and resins. [1] In our day-to-day life we encounter silicone elastomers in applications ranging from highway sealants to contact lenses. Details of the formulation, fabrication and applications of silicone elastomers up to 1978 have been documented by Lynch [2], developments in the 1980's were covered in a series of reviews and monographs from the Dow Corning Corporations elastomers group [3-5] and work into the 1990s was described in a review by Stein from General Electric in 1996 [6]. Thomas reviewed the principal cure chemistries utilised in the preparation of silicone elastomers in 1993 [7].

Theories of rubber elasticity must successfully account for:

(i) Stress-strain behaviour
(ii) Stress-strain behaviour in the swollen state
(iii) Equilibrium swelling behaviour

A number of theoretical developments during the last 25 years have led towards a more rigorous molecular understanding of rubber-like elastomeric behaviour [8-10]. Such theories are increasingly realistic in the treatment of topological features such as junction fluctuations and entangling and also the detailed structural characteristics that distinguish an elastomeric chain of one type from another. On the experimental side, new methods have been developed for the synthesis of elastomeric networks having well defined structures [11,12] and new techniques established for network characterisation. Although experimental studies of the mechanical properties and swelling characteristics remain the most widely used methods for studying polymer networks [10,13,14] information from strain birefringence, strain dichroism, segmental orientation and angle

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neutron scattering investigations is now being utilised to provide a more complete understanding of the properties of elastomeric materials [10].

2. Preparation of Silicone Elastomers

There are a wide variety of methods currently available for cross-linking polysiloxane chains to give elastomeric materials [7]. Many of these approaches give poor control over cross-link densities and also little or no control on the placements and distributions of the cross-link sites. Examples of such random cross-linking methods include peroxide thermolysis [15] or high-energy irradiation [16]. The application of most of the standard polymer characterisation methods after the network is formed is essentially impossible due to the material being intractable, the three-dimensional structure simply results in the material swelling but not dissolving upon immersion in common organic solvents.

There have been considerable efforts over the last twenty years or so to prepare siloxane chains containing functional groups either at the chain ends or as substituents [17]. In the case where the subsequent reactions of these functional groups are stoichiometric and proceed to completion, such reactions have the capability of producing well-defined elastomeric materials [11,12,18-26]. These elastomers may be classified as 'model' networks in the sense that independent information obtained on the network precursor chains can give valuable information on the resulting network structures. One example of such a reaction is the end-linking of hydroxyl terminated PDMS with tetraethoxysilane (TEOS) where the formation of a tetrafunctional cross-link is shown below

\[
4\text{HO-}[\text{PDMS}]-\text{OH} + (\text{C}_2\text{H}_5\text{O})_4\text{Si} \rightarrow \text{HO-}[\text{PDMS}]-\text{Si-}[\text{PDMS}]-\text{OH} + 4\text{C}_2\text{H}_5\text{OH} \quad (1)
\]

where subsequent condensation reactions lead to gelation. In this case, the conventional solution characterisation techniques may be used to determine the number-average molar mass, \( \bar{M}_n \), of the network precursor chains and the distribution about this average, \( \bar{M}_n / \bar{M}_n \). Upon exhaustively reacting the hydroxyl groups with the cross-linking agent, a tetrafunctional network (\( \phi=4 \)) is obtained whereby the molar mass between cross-links \( M_c \) and the distribution of chain lengths between cross-links may be obtained from the independently determined \( \bar{M}_n \) and \( \bar{M}_n / \bar{M}_n \) values for the network chain precursors. A simple substitution of a stoichiometric quantity of triethoxysilane \( \text{RSi(OC}_2\text{H}_3)_3 \) for the TEOS depicted in scheme 1 can be used to prepare the corresponding trifunctional network (\( \phi=3 \)). The use of the hydrosilation reaction whereby vinyl functional siloxane network precursor chains are reacted with the Si-H functionalities in a lower molar mass network junction precursor molecule have also been widely used to give control of the resulting network structures [6,11,27].