Journal of Metals, Materials and Minerals. Vol. 12 No. 2 pp. 7-12, 2003

The Gelation Behaviors and Mechanical Properties of Silicone Resins for A Breast Model Application

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ABSTRACT

In this work, the possibility of using silicone resins to construct a breast cancer training model is examined. A locally available resin that is investigated is RTV 585. The curing agent was varied at different concentrations i.e. 1.0, 1.5, 2.0 and 2.5 phr. An organometallic (tin) catalyst was utilized as a curing agent in the present work. It was found that the curing agent significantly improved the elastomer strength by enhancing the cross-link density of the resulting cured specimens. Furthermore, the modulus as a function of time indicated that the resulting elastomer might take up to 2 weeks at room temperature to render a complete development in the specimen mechanical properties. Elevated temperature was found to significantly reduce the gel time of this silicone resin and the temperature-dependent gelation process of the resin can be well predicted using the Arrhenius model. This study paves the way for the further improvement in the fabrication of the breast model final products based on silicone elastomer.

Keywords : Silicone Elastomer, Breast Model, Breast Cancer, Gelation.

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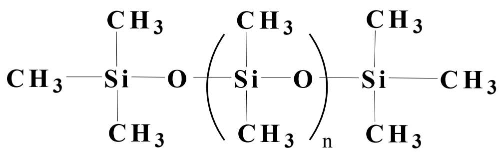
INTRODUCTION

Polydimethylsiloxane (PDMS) or silicones have been utilized extensively for the construction of a wide variety of medical devices owing to its superior stability as well as its outstanding rubber elasticity. At present, silicone finds its way into an extremely wide range of medical and industrial applications. Silicone resin is an inorganic polymer, having properties depending on the molecular weights and alkyl groups in its structure (Smith, 1974).



(n = 0,1,2…..)

The simplest and most widely used silicones are polydimethylsiloxanes. The resins have been put into practical use in various fields including medication. One of the medical devices, that we investigated, is a breast cancer training model.

The statistics on the number of women diagnosed with breast cancer in Thailand are difficult to pin down. In Bangkok, it's estimated that just over 20 women in every 100,000 will be diagnosed with breast cancer (http ://W3.whosea.org). A breast cancer training model can be used as a teaching aid for self-examination and detection of breast cancer symptoms. Furthermore, breast cancer training models, which are designed for training across a range of applications including self-diagnosis and procedures for nurses, doctors and specialists, are mostly imported from Japan, Europe or America. This model possesses relatively low strength and durability and is still far from realistic. Moreover, the imported one typically costs more than 30,000 baht per piece which is rather expensive to be affordable to medics or a local hospital. In this investigation, types of locally available silicone resins, composition of breast model, gel time, and aging phenomenon of silicone elatomers were studied. The major components of this resin system consist of (i) silicone resin (ii) silicone fluid and (iii) curing agent. The main objectives of this study are to determine the relationship of rheology and the mechanical properties of silicone elastomer, which can yield the most durable and realistic breast-training model.

EXPERIMENTAL

Materials

The silicone elastomer system is composed of silicone resin, silicone fluid, and a curing agent (catalyst). The study was carried out on four different silicone resins: RTV 585, RTV 300, RTV 3480, and RTV 4503. All types of silicone resins that were used in this system are room temperature vulcanization systems (RTV). The typical characteristics of each silicone types are shown in Table 1.

Table 1 Fundamental characteristics of commercial silicone resins.

Characteristics	RTV 585	RTV 300	RTV 3480	RTV 4503
Appearance	viscous liquid	viscous liquid	viscous liquid	viscous liquid
Colour	beige	white	pale gray	white
Density, 25°C (g/cm^3)	1.22	1.10	1.33	1.17
Viscosity, 25°C (mPa.s)	45,000	50,000	35,000	40,000
Cost (Baht/kg)	630	600	900	800

Tensile Measurements

Test specimens were prepared according to ASTM D412, as illustrated in Figure 1. The tensile properties of specimens were determined by using a universal testing machine (LLOYD 2000R) with a load cell of 1 kN. The crosshead speed was 500 mm/min. Reported tensile properties were based on the mean of at least three samples for each composition. The results of the maximum tensile strength, percent elongation at break and modulus of elasticity were reported.

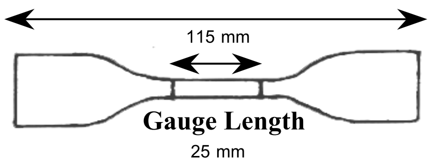


Figure 1 Standard Dies for cutting dumbbell specimen

Rheological Measurements

Rheological measurements were conducted using a computer-controlled Haake RS75 rheometer in a cone and plate geometry. The top plate is a cone of 3.5 cm in diameter with a 0.017 radian (1^o) cone angle and gap 0.052 mm. The curing process of a silicone resin can be followed by performing a time sweep of a dynamic oscillation measurement at a specific frequency of 1 Hz. The strain amplitude was set to be 2.5×10^{-2}. The storage modulus (G′), and loss modulus (G″) were continually monitored as a function of time. All experiments were conducted at room temperature.

RESULTS AND DISCUSSION

The property comparison of silicone resins used to fabricate a breast model is shown in Figure 2. The effect of silicone resin types on their stress-strain behaviors at a constant curing agent concentration of 1.5 phr in the fully cured stage was illustrated. It was observed that the tensile strength and percent elongation of RTV 585 were better than any other silicone resins.

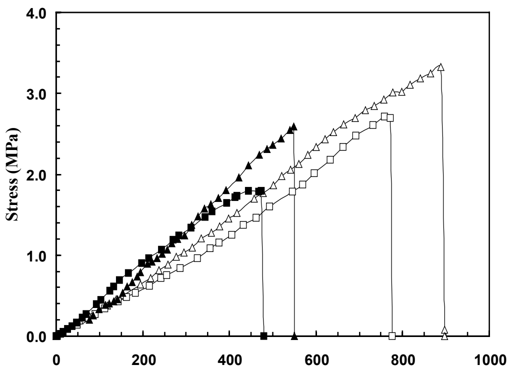


Figure 2 Effect of silicone resin types on stress-strain behaviors at constant curing agent concentration of 1.5 phr after three weeks (–△–RTV 585), (–□–RTV 300),(–■– RTV3480), (–▲–RTV 4503)

These properties are the important factors for fabricating a breast-training model. Our experimental results revealed that the elastic modulus of the silicone elastomer used was comparable to that of human breast tissue (Azar, 2001). As a consequence, RTV 585 was chosen as a model resin for the rest of the study.

Figure 3 exhibits a tensile modulus of silicone resin RTV 585 at various curing agent concentrations. It was observed that the tensile modulus sharply increases with curing time in the first two weeks at room temperature and became relatively stable after that. The elastomer's moduli were also found to increase with curing agent concentration when compared at the same reaction time. The network formation of this RTV; therefore, requires at least two weeks to yield a fully developed polymer network and is the justification for a suitable processing condition. The presence of a greater amount of curing agent will increase the junction points of the elastomer network thus render the higher

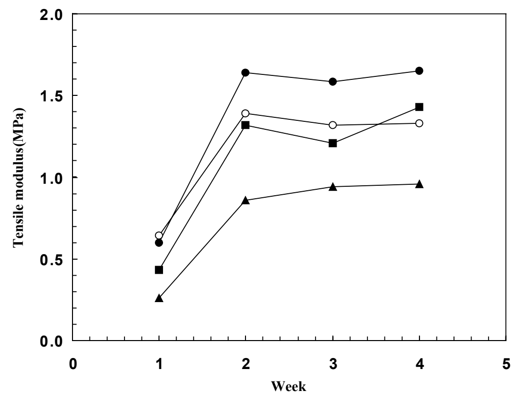


Figure 3 Tensile modulus of silicone resin RTV 585 as a function of curing agent concentration
(–▲–curing agent 1.0 phr),
(–■–curing agent 1.5 phr),
(–○–curing agent 2.0 phr),
(–●–curing agent 2.5 phr)

modulus through out the course of the curing reaction as clearly seen in the figure. Though it seems that the elastomers were cured at about the same reaction rate i.e. within two weeks, independent of the curing agent concentration, this is maybe due to the relatively large time scale used in the graph.

According to the classical theory of rubber elasticity, the crosslink density can be calculated by the relationship shown in equation 1 (Bikales, *et al.* 1988):

$$\nu = \frac{E}{3RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1)$$

where E is the modulus (Pa), ν is the average crosslink density (mole/cm3), R is the gas constant, and T is the temperature (Kelvin). Figure 4 suggests an increase in crosslink density with increasing curing agent concentration. Moreover, crosslink density was developing as the curing reaction proceeded and became stable after 2 weeks. The specimen using a curing agent concentration of 1.5 phr was found to be the most suitable composition with approximately 0.8×10–4 mole/cm3 in its crosslink density.

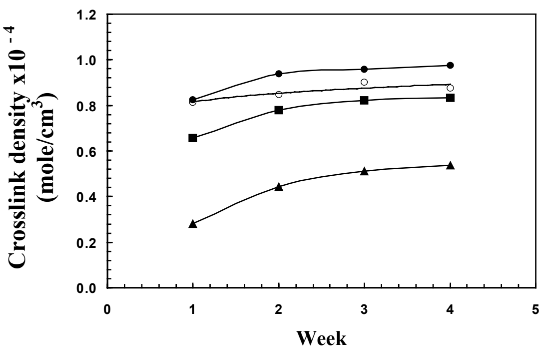


Figure 4 Crosslink density of RTV 585 as a function of curing agent concentrations
(-▲- curing agent 1.0 phr),
(-■- curing agent 1.5 phr),
(-○- curing agent 2.0 phr),

One major objective of this study is to use a rheological technique as a tool to determine the sol-gel transition, or gel point, of silicone resin. Figure 5 presents the effect of silicone oil (350 mPa.s, 25°C) concentration on the gel time of RTV 585 at various curing agent concentrations. The result revealed that the resin's gel time increased as the silicone oil (modifier) increased. This can be explained as due to the fact that the silicone oil, which is a non-reactive component, suspends in the silicone resin showing the dilution effect on the resin mixture resulting in retardation of the network crosslinking reaction. Generally it can be seen that the change in gel time strongly depends on the concentration of the curing agent. In this study, it was observed that the gel time of the curing agent at 1.5 phr. was similar to the gel time with 2.0 phr of curing agent. On the other hand, it took a much longer time when the amount of curing agent was reduced to 1.0 phr. Therefore, the amount of 1.5 phr of the curing agent is about the optimum point or the stoichiometric concentration of this silicone. To obtain a reasonable curing time, the suggested amount of curing agent was; therefore, 1.5 phr.

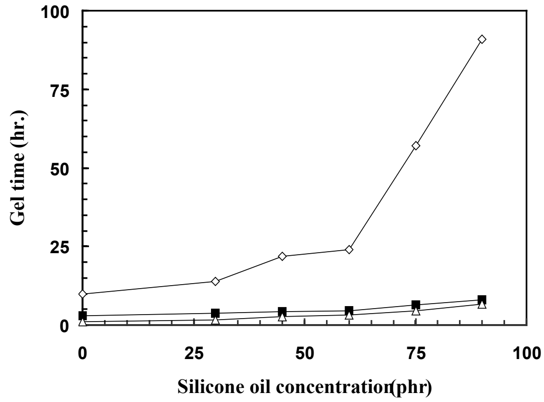


Figure 5 Effect of silicone oil concentration on gel time of silicone resin RTV 585 at various curing agent concentrations
(-◇- curing agent 1.0 phr),
(-■- curing agent 1.5 phr),
(-△- curing agent 2.0 phr), ASTM D2471

In Figure 6, the storage modulus (G′) and the loss modulus (G″) at a fixed frequency (1 Hz.) as a function of curing time are depicted. In this study, the G′-G″ crossover was used as a gel point. At this point, G′ surpasses G″ though both moduli keep increasing steadily. However, the increase of G″ becomes relatively slower compared to G'. Beyond the gel point, the elastic effect dominates the forming network, which is capable of storing elastic energy. This is the reason why G′ increases and finally overcomes G″ as the curing proceeds past the gel point. Eventually, G′ levels off steadily as the sample becomes completely cross-linked by chemical bonds. The gel time of our RTV 585 from this plot is 11,200 seconds.

Figure 7 shows the effect of temperature on gelation of silicone resin RTV 585 at a constant curing agent concentration of 1.5 phr. The gel time decreases when curing temperature increases. This means that temperature can

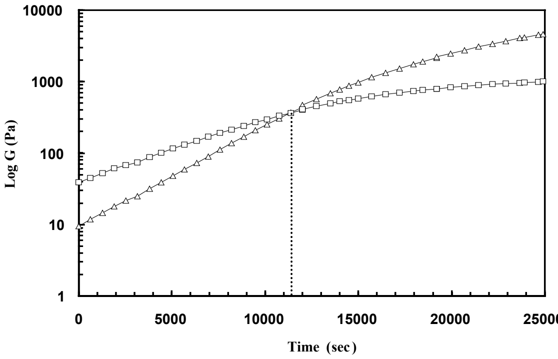


Figure 6 Dynamic moduli as a function of time for silicone resin RTV 585 at curing agent concentration of 1.5 phr
(-△-storage modulus), (-□-loss modulus)

significantly accelerate the curing process of this silicone elastomer. This behavior is also found in other RTV systems and is useful in some applications to optimize the processing time (Bhowmick and Stephens, 1988).

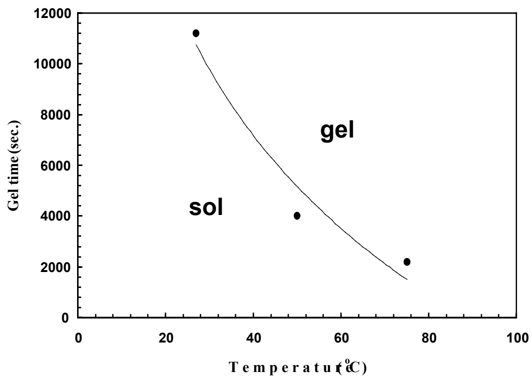


Figure 7 Effect of temperature on gelation of silicone resin RTV 585 at curing agent concentration of 1.5 phr

From the above results, it was evident that temperature can accelerate the gelation of silicone elastomer. An Arrhenius model is frequently used to predict the temperature dependence of a gelation process of crosslinked polymer networks (Diachun, 1994; and Rimdusit, *et al.* 2002). The relation between gel time, t_{gel}, and temperature is given by equation 2:

$$t_{gel} = Ae^{-\frac{\Delta E}{RT}}$$

$$\ln(t_{gel}) = \ln A + \left(-\frac{\Delta E}{RT}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots 2)$$

where A is a frequency factor (constant), ΔE is the activation energy with units of kJ/mol, R is the gas constant, and T is the temperature in Kelvins.

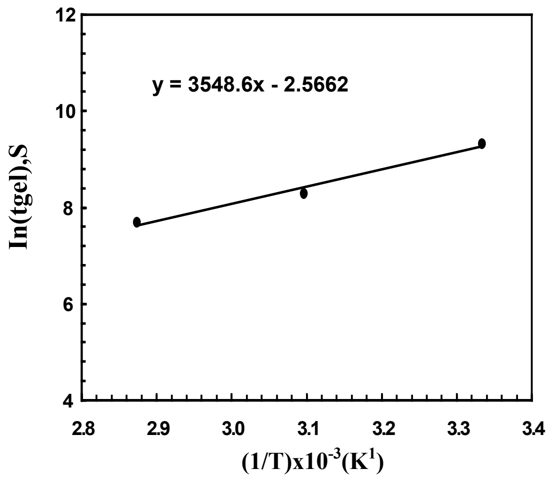


Figure 8 Arrhenius plot of the gelation behavior of silicone resin RTV 585 at a curing agent concentration of 1.5 phr.

The arrhenius plot of this gelation process in Figure 8 shows a linear relationship of the gelation process of this silicone elastomer. The plot yields the factor (A) = 7.768×10^{-2} s and the activation energy, ΔE = 29.5 kJ/mol. The values are in good agreement with those of typical RTV resins reported elsewhere (Stein, 1992). Therefore the gel equation for predicting the gelation process of our silicone elastomer at the desirable temperature can be given by the following equation 3:

$$t_{gel} = 0.07768\, e^{\frac{-29.5}{RT}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3)$$

CONCLUSIONS

The mechanical properties of the silicone RTV 585 used for breast model applications required up to two weeks to render a fully developed polymer network. It was found that the curing agent significantly improved the elastomer strength by enhancing its cross-link density of the resulting cured specimens. Elevated temperature was found to significantly reduce the gel time of this silicone resin and the temperature-dependent gelation process of the resin can be well predicted by the Arrhenius model.

ACKNOWLEDGMENTS

This research is supported by the Rajchadapisek Fund of Chulalongkorn University of the fiscal year 2003. The authors would like to acknowledge the Department of Chemical Engineering, Faculty of Engineering, Burapha University and its technical staff for the rheological experiment. The Development Grant for New Faculty/Researchers of Chulalongkorn University to one of the authors, S.R., is also gratefully acknowledged.

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(Revised version accepted April 1, 2003)