

Dynamic mechanical properties of networks prepared from siloxane modified divinyl benzene pre-polymers

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Abstract

Pre-polymers prepared by modifying divinyl benzene by introducing dimethyl siloxane units of different chain lengths were polymerised with divinyl benzene using free radical initiators. The dynamic mechanical properties of the resulting networks were studied. The DMA curves were interpreted based on the reaction mechanism obtained using FT-NIR and ESR spectra. The peak widths of the loss modulus and $\tan \delta$ curves were interpreted considering the crosslinking reactions in the pre-polymer/divinyl benzene mixtures and micro gelation resulting from the crosslinking. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Pre-polymers; Loss modulus; $\tan \delta$ curves

1. Introduction

There are many applications which require polymers with excellent clarity and mechanical properties. The thermosets from diethylene glycol bis allyl carbonate (CR39) resin have enjoyed this position for many years in various optical applications. However, there is a need to develop new monomers with improved properties to control better the manufacturing process and to be competitive in the market. This work was targeted towards developing new monomers and resulting polymers with better properties, determining optimum polymerisation conditions [1] and evaluating dynamic mechanical properties of the polymers.

The glass transition (T_g) is one of the most important properties exhibited by a polymer, determining its physical state and influencing other properties such as rheological characteristics, mechanical stiffness and toughness [2]. Below its T_g a material is brittle, whereas it is ductile, leathery or liquid above its T_g . The damping properties of a polymer are dominated by its T_g . When the chain segments in a polymer backbone undergo de Gennes [3] reptation motions, molecular vibrational energy is converted into heat energy and a loss peak appears in a certain temperature

range. Usually the temperature range of the glass transition region in a homopolymer is about 20–30°C. There are several methods to increase the width of the transition region through polymer blends, interpenetrating networks, and highly crosslinked networks. Similarly a convenient method to adjust the position of the T_g according to a given application is to copolymerise monomers A and B in a certain ratio A/B. The monomers are chosen in such a way that the T_g values of the two homopolymers lie above and below the required glass transition temperature.

The glass transition temperature of linear polymers as a function of monomer composition and molecular weight are generally well understood [4]. On the other hand, the T_g region of a thermoset polymer is not so clearly understood in terms of specific molecular factors. The most common approach is to relate the T_g of a crosslinked system to the overall conversion [5], although it is accepted that the variation in T_g is attributed to various molecular parameters such as the molecular weight, the stiffness and the free volume entrapped in the network. It has been observed [6] in epoxy systems that the increase of the molecular weight by linear polymerisation is the main factor contributing to the increase in T_g before gelation, while after gelation, T_g is effected by a decrease in the free volume and/or an increase in the stiffness due to the crosslinking reactions.

Methyl methacrylate and diethylene glycol bis allyl carbonate are well known monomers used in the optical polymer industry, and, as a result, its polymerisations and

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Table 1
Characteristics of pre-polymers

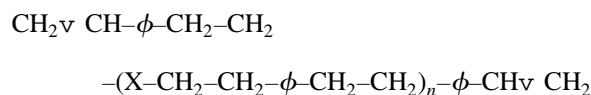
Pre polymer	DVB unreacted (%)	Average chain length
DST30	30	1
DST10	10	4
DST3	3	8

copolymerisations with crosslinking methacrylate monomers have also received extensive attention [7,8]. In addition to this, many papers have been published in recent times on the free radical crosslinking polymerisations of divinyl monomers, and this work has been reviewed recently by Matsumoto [9]. The free radical crosslinking copolymerisation of styrene and divinyl benzene also has received [10–13] much attention during the last fifty years, as a result of the importance of these copolymers in Size Exclusion Chromatography and ion exchange resins.

The use of divinyl monomers in the free radical polymerisations cause crosslinking. When a polymer radical propagates with the double bond of a divinyl monomer, first the unreacted double bond of the same monomer molecule becomes pendant on the chain. If a second polymer radical adds to this double bond a crosslink will be formed which will ultimately cause a gel/network formation. There are several characteristic features [9] of crosslinking polymerisations: early onset of the Trommsdorf effect, incomplete conversion of the double bonds due to vitrification and post polymerisation reactions of trapped radicals with oxygen.

Network polymers of divinyl benzene (DVB) are brittle materials. They form densely crosslinked polymer networks containing untreated double bonds particularly with higher DVB contents. Therefore, with a view to reducing the residual double bond concentration and to improve properties such as impact resistance, the DVB monomer was modified [14] with dimethyl siloxane to obtain a set of flexible pre-polymers which will be called DST in the proceeding discussion. Siloxane modified divinyl benzene (DST) has

the general structure



where X is $\text{Si}(\text{CH}_3)_2\text{-O-Si}(\text{CH}_3)_2$ and the value of n in the pre-polymer varies from 1 to 8.

This pre-polymer was then copolymerised with divinyl benzene initiated with a free radical initiator. The polymerisation kinetics of these systems were discussed in our previous paper [1]. Dynamic mechanical properties of the resulting polymers are presented in this paper.

2. Experimental

2.1. Materials and sample preparations

The initiators benzoyl peroxide (BPO) and azo-iso-butyronitrile (AIBN) were purified by re-precipitating into methanol from a chloroform solution. The liquid initiator, *t*-butyl peroxy-2-ethyl hexanoate (TBPEH) was used as received without additional purification. The DST pre-polymers were synthesised by Matisons et al. [14] at the University of South Australia, and their characteristics are given in Table 1. The inhibitor in the pre-polymers, DST, and pure DVB were removed by passing the liquid monomers through a neutral alumina column. Gel Permeation Chromatography was used to confirm that there was no change in the composition of the oligomers after passing them through the column. The DVB was provided by the SOLA International, Adelaide, Australia, and it was a mixture of para and meta DVB(97%) and ethyl vinyl benzene(3%). Mixtures of the initiator, DST and DVB were made up to the proportions given in Table 2, and samples of these mixtures were placed in 5 mm glass tubes for FT-NIR or in 3 mm quartz tubes for ESR studies. These samples were degassed through three freeze thaw cycles, after which they were sealed under vacuum.

Table 2
Polymerisation mixtures and conditions

Pre-polymer mix	Temperature at maximum tan δ ($^{\circ}\text{C}$)	tan δ width ($^{\circ}\text{C}$)	tan δ_{max}	Storage modulus above T_g ($\text{Pa} \times 10^9$)
DST30	75	146	0.1	1.0
DST10	0	64	0.26	
DST10-15	0	74	0.21	
DST10-20	0	82	0.18	
DST10-30	10	148	0.17	0.6
DST10-44	20	144	0.16	
DST3-10	-15	28	0.5	
DST3-15	-15	38	0.35	
DST3-20	-15	50	0.25	
DST3-30	-15	114	0.125	
CR39	90	78	0.18	0.7

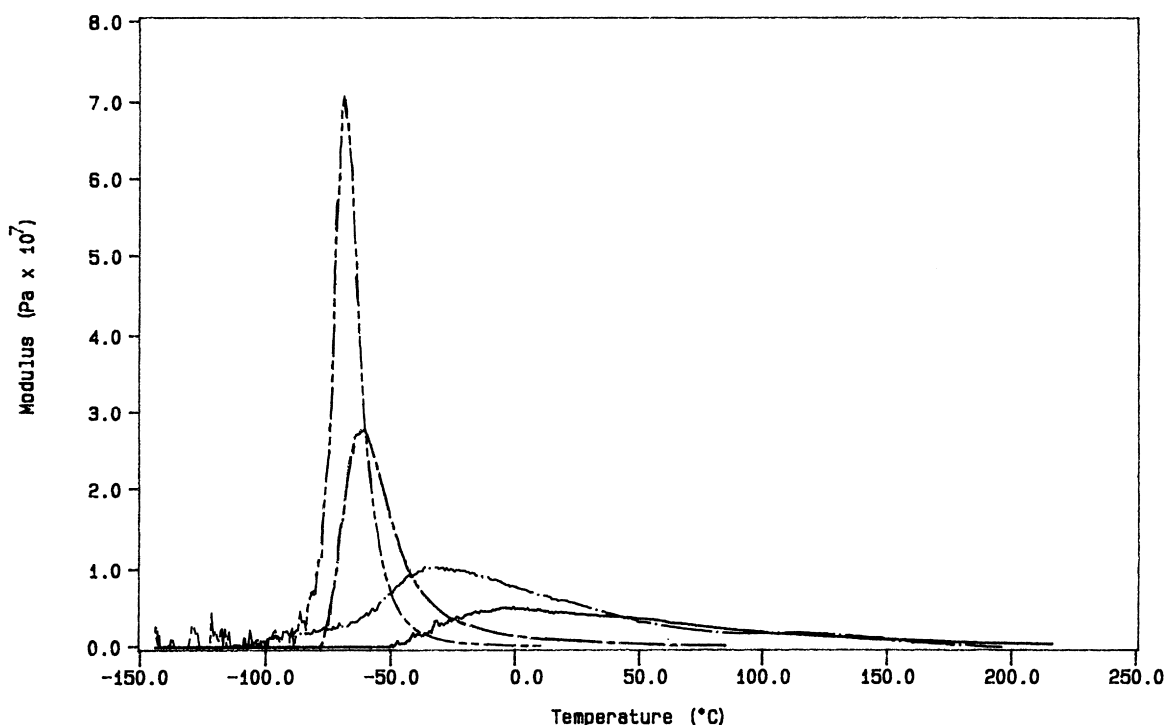


Fig. 1. Loss modulus curves of (---) 42%, (— — —) 57%, (— · —) 79% and (—) 90% reacted DST30 mixture.

2.2. Polymerisation

The FT-NIR technique was used [1] to follow the conversion of monomer into polymer since previous workers [7,8,15] have successfully demonstrated the use of this technique to monitor monomer conversion in polymerization or copolymerization processes. The NIR spectra obtained were accumulated over 16 scans in every 2 min at a resolution of 2 cm^{-1} using a Perkin-Elmer 1600 spectrometer fitted with an external bench and MCT detector. After determining the polymerisation conditions, the samples were polymerised using similar conditions in a block heater. At the end of the reaction time, the samples were quenched in liquid nitrogen and kept at liquid nitrogen temperature until they were ready to be used for DMA studies.

2.3. Dynamic mechanical analysis

A Perkin-Elmer DMA7 instrument was used in the parallel plate mode on a sample of approximately 3 mm width and 1.5 mm height or in the three point bending mode on a sample approximately 3 mm in diameter and 15 mm long. Temperature/time scans or stress/strain scans were carried out at a frequency of 1 Hz. A heating rate of 5 K min^{-1} was used for the temperature/time scans. Normally the T_g value is taken as the point of deflection of the $\tan \delta$ curve from the base line. However, this was difficult in some samples due to the appearance of shoulders in the $\tan \delta$ peak. In those cases the temperature at the maximum point of the loss modulus peak was taken as the measure of T_g .

3. Results and discussion

The characteristics of the DST pre-polymers are given in Table 1. They all contained a significant amount of unreacted monomer, DVB, as confirmed by GPC measurements. Each pre-polymer was given a symbol to indicate the amount of unreacted DVB. For example, DST30 means that there is 30% unreacted DVB in the mixture. The average length of the siloxane chain in the pre-polymers was indicated by the value for n , which is given in Table 1. The pre-polymer with the lowest chain length (DST30) contained the highest amount of unreacted DVB. As the chain length increased, the viscosity of the pre-polymers also increased. Each of the pre-polymers was mixed with extra DVB to give various amounts of free DVB in the polymerisation mixtures. These mixtures were labeled DST_{x-y} , where x indicates the type of the pre-polymer (DST3, DST10 and DST30) and y indicates the total amount of DVB in the mixture after addition of the extra DVB.

In the systems under investigation here, both monomers contain two double bonds. But in the DST the double bonds are separated by the siloxane chain. Therefore, the crosslinks formed by the DST units have a lesser effect in restricting the mobility of the molecules than those formed by the DVB units. Previous studies of polymerisations of dimethacrylates of different chain lengths have shown [16] that an increase in the spacer length between the double bonds increases the polymerisation rates, and the final conversions are higher. The dimethacrylate reactions were found to be inhomogeneous, involving micro regions of high crosslink

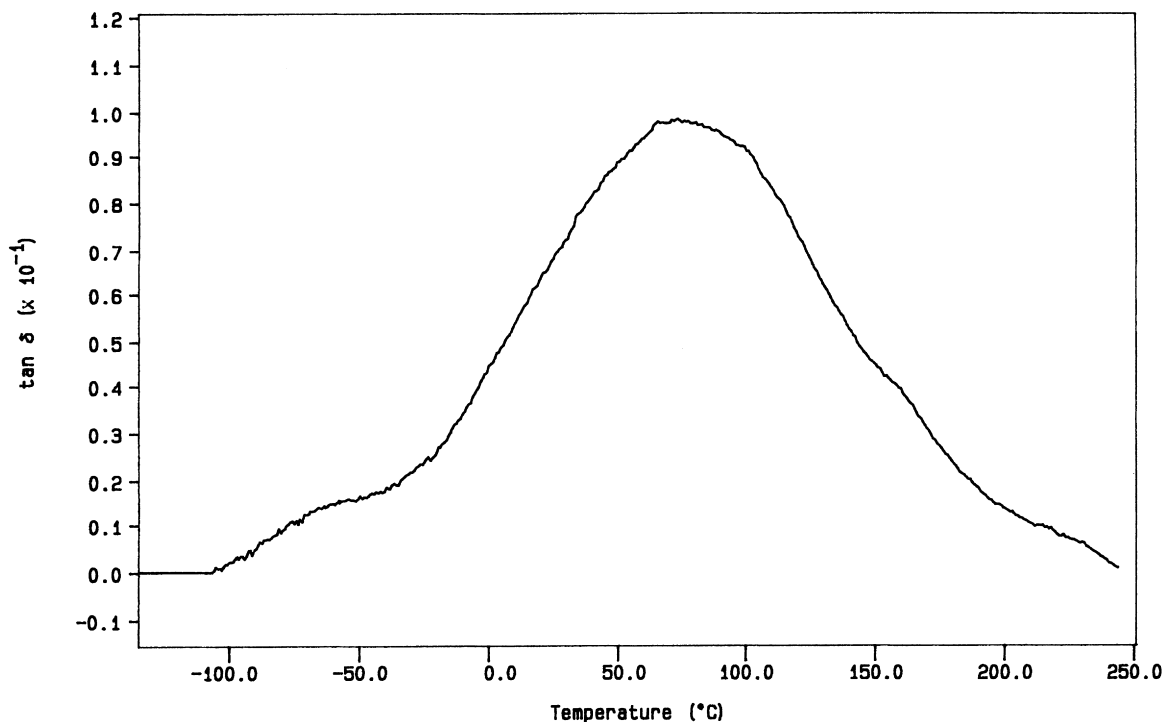


Fig. 2. DMA curve for 95% polymerised DST30.

density surrounded by regions of low crosslink density [17,18]. The resultant morphology was found to be a function of the spacer length in the monomer. These studies have also reported sample cracking during the polymerisation of

some dimethacrylates. No such problems were encountered in any of the samples studied in this work.

During the polymerisation of these DST systems, auto acceleration was found to occur [1] at a very early stage

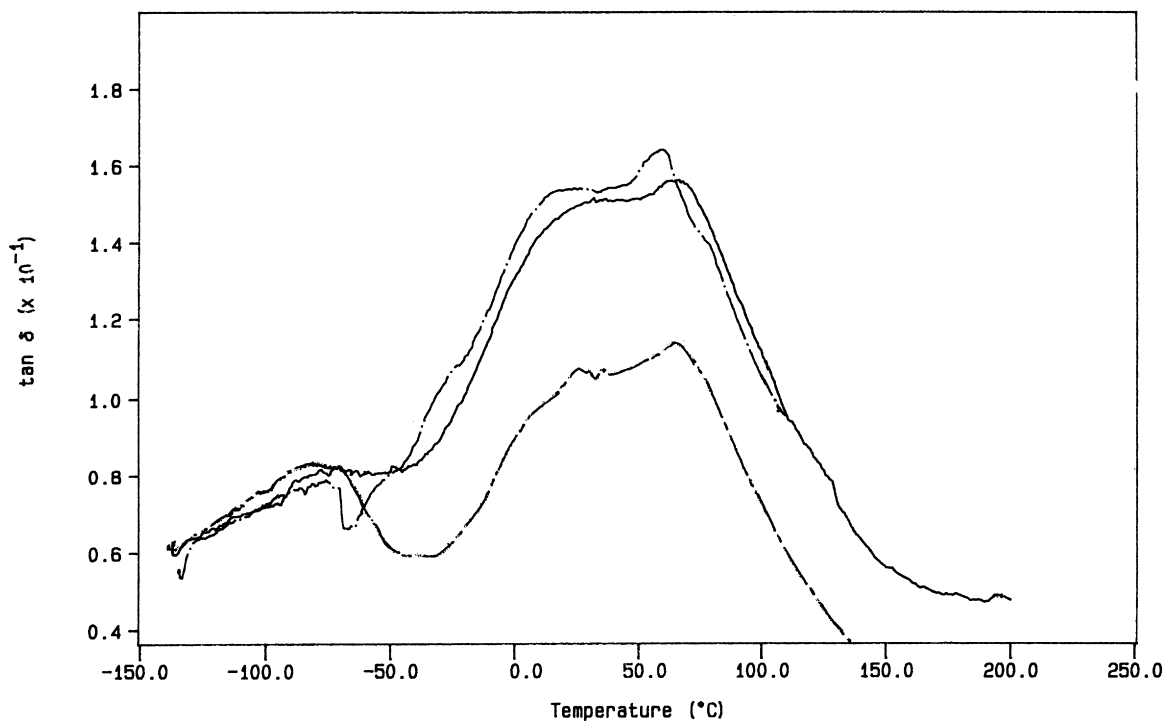


Fig. 3. The tan δ curves for DST30 polymerised at (— · —) 3% BPO at 90°C, (—) 3% BPO at 70°C and (— - —) 2% AIBN at 50°C.

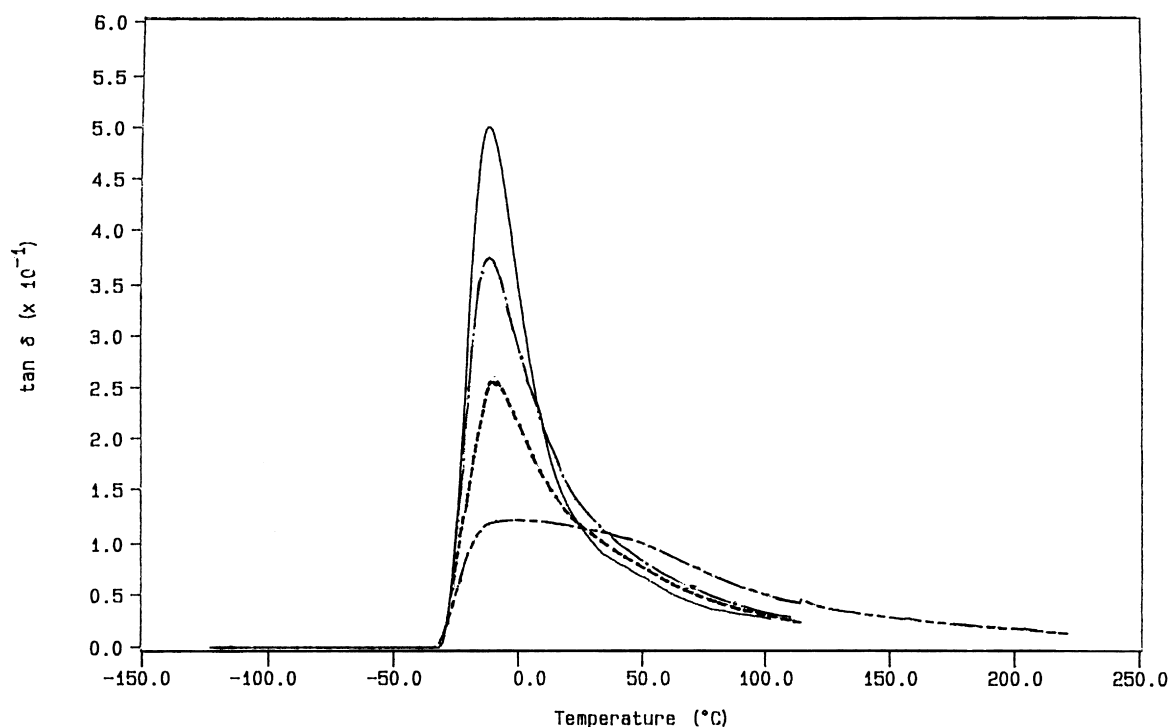


Fig. 4. The $\tan \delta$ curves for DST3 with (—) 10%, (— · —) 15%, (---) 20% and (— — —) 30 % DVB contents.

of the polymerisation. In fact, except for DST10, DST30 and DST30-44, all other polymerisations studied showed auto acceleration from essentially zero conversion. The final extent of cure for isothermal conditions was estimated from the flat portion of the conversion-time curves. Physical ageing phenomena [19] did not contribute to an increase in the final extent of cure. However, the final extent of cure did depend on the reaction temperature and the amount of DVB in the mixture. DST3-10, DST3-15 and DST10 reached 100% conversion. The final conversion did not depend on the spacer length in the pre-polymer. For example, DST3-30, DST10-30 and DST30 all reached 90% final conversion at 70°C.

The plots of loss modulus versus temperature for the reaction mixture with 1.33% TBPEH/DST30 cured at 80°C to different conversions are given in Fig. 1. The samples show a gradual increase in the width of the loss modulus curve with conversion, and there is a major increase in the peak width between 57–79% conversion. A gradual broadening of the loss modulus curve with increasing crosslinking density has been reported previously [20]. This broadening has been explained as being due to an increased width or breadth of the network chain distribution. Since the average chain length between crosslinks in the system investigated here depends on the relative rates of addition of DVB and DST molecules, the increased width of the loss modulus curve also indicates a change in the relative rate of addition of the two monomers over the polymerisation range. Therefore, the broadening of the loss modulus curve should be due to the heterogeneity intro-

duced in the system as a result of a change in the relative rates of addition or may be due to microgelation. The crosslink density is not the same in all sections of the network, and thus the radicals in the highly crosslinked sections may become trapped. This may also result in non-uniform formation of crosslinks, which will increase the network chain distribution as the reaction proceeds. Fig. 1 also shows an increase in the T_g with conversion for DST30 prepolymer. This increase may be caused by several factors: consumption of monomer and pendant double bonds, and an increase in the crosslink density, which causes a reduction in the mobility of the polymer chains.

The DMA curve for the DST30 sample polymerised to 95% conversion is shown in Fig. 2. This sample was polymerised at 90°C with 1.33% TBPEH. These measurements were carried out using the 3-point bending mode. Therefore, there is a better resolution in the curves compared to the results obtained using the parallel plate mode. The $\tan \delta$ curve is very broad with a peak at 95°C, which, as in polymerised CR39, corresponds to the T_g (the α transition) in the polymer. The broad shoulder at 50°C may be due to the motions associated with the siloxane group. The DMA curves for polymerised CR39 show [21] a broad peak at about -75°C and a shoulder on the α relaxation at about 10°C, which has been assigned to the flexible spacer in this monomer.

Fig. 3 shows the $\tan \delta$ curves for DST30 samples cured with 2 and 3% AIBN and BPO at 50, 70 and 90°C respectively, for 70% conversion followed by a 30 min post cure treatment at 110°C. The samples are about 95% conversion.

The figure shows that in the sample cured using AIBN at 50°C, there were two well separated peaks, whereas in the other two samples the peak at about -75°C shows only a shoulder on the main peak. This indicates that in the AIBN initiated sample, there are two regions, one a soft region and the other a hard region, with clearly defined boundaries. It is also observed that in the AIBN initiated sample, the main peak between -25 and 100°C has a lower $\tan \delta_{\max}$. This indicates that the region giving rise to this peak is more densely cross-linked than the BPO sample. The greater heterogeneity observed in the AIBN initiated samples may be due to higher reaction rates.

The $\tan \delta$ curves for DST3 with different amounts of DVB are shown in Fig. 4 and the data derived from the figure are given in Table 2. The $\tan \delta$ peaks of the samples are not symmetrical. Symmetrical $\tan \delta$ curves were observed [22] for the homopolymerised networks of the urethane acrylates. The loss of symmetry in the networks of the current study is due to the presence of the DVB monomer. The temperature at $\tan \delta_{\max}$ does not change in DST10 until the DVB content is 10%, and for DST3 this temperature does not change even at 30% DVB. However, the width of the $\tan \delta$ curve increases with the DVB content in both the pre-polymers. While the lower temperature end remains the same, the upper temperature end increases with the DVB content. The observation that the lower temperature end remains the same indicates that the T_g of the siloxane segments are not effected by the crosslink density in DST3 and in DST10 upto a certain crosslink density. In both DST3 and DST10, the increase in the peak width is significant for the DVB contents between 20 and 30%. The $\tan \delta$ curve widths for DST10-30 and DST30 (both systems with the same DVB content) are similar. However, the $\tan \delta$ curve in DST3-30 is narrower than in DST10-30 and DST30. This indicates that the increase in the peak width of these systems is mostly due to microgelation and heterogeneity results from this rather than to changes in crosslink chain distribution.

The rate parameter data [1] indicate that this polymerisation reaction is heterogeneous. The system reaches the gel point at a very early stage of the polymerisation due to the preferential reaction of the DVB monomer. As the crosslink concentration increases, the propagation rate coefficients drop. During the second stage in DST3-10, for example, the pre-polymer units start to react. However, due to the flexible siloxane segment in the monomer, the reaction does not further tighten the network. As a result, there is no further drop in the value of the rate coefficient upto about 60% conversion.

More radicals are formed [1] in the systems with higher DVB contents. Because of the higher double bond concentrations and the consequential increased crosslinking, there is a greater trapping of radicals. With an increase in the DVB content, the microgelation increases as the rate of

polymerisation is increased. This results in a broadening of the $\tan \delta$ peak in the samples with higher DVB contents. The peak width for a cured CR39 resin is also compared with the widths of other monomers in Table 2. The curve widths for these pre-polymers with more than 30% DVB are much broader than the curve for the cured CR39 resin.

The intensity of the $\tan \delta$ peak at the T_g temperature reflects the extent of mobility of the macromolecular chain segments at this temperature [23]. Since crosslinks restrict main chain mobility in the polymer, one would expect that the area under the loss modulus curves vs temperature would increase with a decrease in the crosslink density. This trend will be reflected in the intensity of the $\tan \delta$ peak. The $\tan \delta_{\max}$ value which corresponds to the crosslink density is also given in Table 2. The increase in the DVB content increases the crosslink density and correspondingly reduces the $\tan \delta_{\max}$ value in both DST10 and DST3. Comparison of the $\tan \delta_{\max}$ values between the three pre-polymers with the same DVB contents, indicate that the increase of pre-polymer molecular weight from DST30 to DST10 reduces the crosslink density, as expected. But between DST10 and DST3, the increase in the pre-polymer molecular weight increases the crosslink density. This is due to possible chain entanglements with an increase in the molecular weight. The amount of physical chain entanglements is independent of the amount of DVB. This may be the reason why the T_g of the siloxane segments are not effected by the amount of DVB present. The rubbery modulus values, which are also shown in Table 2, compliment the relationship observed with the $\tan \delta_{\max}$ values. The physical chain entanglement phenomena was also confirmed [1] from the radical decay curves during post curing.

4. Conclusions

There is a gradual increase in the width of the loss modulus curves during the polymerisation reaction. Samples cured with AIBN as the initiator show structures with clear boundaries between a soft and a hard phase. The $\tan \delta$ curves observed are not symmetrical. An increase in the DVB content increases the width of the $\tan \delta$ curve; however, the lower temperature end remained unaltered. All these observations indicate the presence of microgelation in some of the samples.

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