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Bimodality and Increased Amount of Crosslinker Enhances Tensile Properties of the Silicone Networks

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Abstract: The effect of bimodality i.e. blending short and long chain (0 to 80 % w/w) silicone prepolymers, and that of concentration of the crosslinker on the tensile properties such as percent elongation at break (%Eb), ultimate tensile strength (UTS), 100 % modulus and elastic modulus (E) has been investigated. It was found out that the greater amount of crosslinker used for crosslinking provide an additional reinforcement to the silicone network whereas bimodality further significantly accentuates this effect. Remarkably, the %Eb of the silicone networks was found to increase to an average of 2.4 times than that of the monomodal network, cured in each of the three series of bimodal networks cured with 3.9, 9.1 and 12.3% of crosslinker. The optimum property in each case was observed at about 70 mol % of P100. The over all order of sensitivity of these properties up to about 70 mol % of short chain prepolymer has been observed to be as: %Eb > UTS > 100% modulus > elastic modulus. It has been shown that in addition to the previously published reports the tensile properties are acutely dependent not only upon the degree of crosslinking and primary molecular weight; but also on bimodality and crosslinker concentration for preparation of the unfilled silicone polymer networks. The concept of phase inversion (or phase transition) associated with the optimum properties in polymer blends has for the first time been applied to the bimodal polymer networks. It has been observed that the maxima in tensile properties generally corresponds to phase inversion which takes place at 0.5 volume fraction (70 mol %) of short chain (P100) prepolymer which is in accordance with the literature for other systems.

Introduction

Tensile strength is the mostly measured properties among the physical properties of polymer networks due to its obvious importance. Apart from the nature of polymer, this property of polymer networks is mainly dependent upon the degree crosslinking, the molecular weight and its distribution. Introducing bimodality in a polymer is one way to vary molecular weight distribution of the base polymer. The bimodal polymer networks defined as consisting of short and long chains prepolymers of the same nature has been reported [1-4] to possess combination of good mechanical properties, such as tear energy, tensile behaviour and resilience. The improvements in these properties are thought to originate by creating domain of high crosslink density with in the polymer networks by blending short chains with the long chain before curing. The low incidence of chain irregularities and the non-Gaussian effect which arise from the limited chain extensibility of the short chain prepolymer component with in the bimodal polymer networks have been reported to be responsible for improvement in mechanical properties [5, 6]. The domains of high crosslink densities with in the polymer networks support the applied stress, thus hiding the imperfections and flaws which are more exposed in monomodal polymer networks. The longer chains with in the polymer networks provide higher tear energy in accordance with the Lake-Thomas equations [7]. A good deal of work has been carried out [8-14] earlier to prepare such improved polymeric networks not only associated with silicone but this technology has also been extended to some other systems such as polyisoprene [15] and polyethylene [16].

In the present work, the effect of bimodality and that of concentration of a trifunctional crosslinker have been extended to tensile properties i.e. percent elongation at break (%Eb), ultimate tensile strength (UTS), 100 % modulus and elastic modulus (E) of silicone networks.

Results and discussion

Three different amounts (3.9, 9.1 and 12.3 %) of the same crosslinker i.e. vinyltris (ethoxymethoxy) silane have been used for curing of the bimodal silicone series. First assuming both the silicone prepolymers to be essentially terminally (bi) hydroxyfunctional and of the molecular weight as quoted by the manufacturers, the ratio r of alkoxy groups of the crosslinker to the hydroxyl groups of silicone was calculated. This ratio (r) showed variation from about 18.9 to 1 for 3.9 % of crosslinker, 47 to 2.3 for 9.1 % and 66 to 3.25 for 12.3 % of crosslinker for the bimodal series having 0-80 % short chain prepolymer. In the light of the experimental results and these calculations, the bimodal compositions do not show complete curing when the value of r is less than about 3 i.e. the concentration of crosslinker needed for curing the particular composition is around 3 times the stochiometric amount. The excessive amount of crosslinker required for curing these compositions suggests that the prepolymers probably have more than two functional groups along the chain.

Tab. 1. Variation of Tensile Properties of Bimodal Silicone Networks Cured with 3.9 % crosslinker.

P100		r = [OR]/[OH]	$\upsilon \times 10^{19}$	% Eb	UTS (MNm^{-2})	100 % Modulus (MNm^{-2})	E MNm^{-2}
Wt. % P 100	Mole % P 100						
0	0	4.544	4.089	158	0.425	0.398	0.61
4	18.17	3.597	4.104	210	0.55	0.421	0.61
8	31.69	2.978	4.117	270	0.589	0.360	0.56
10	37.21	2.741	4.003	348	0.571	0.351	0.56
14	46.48	2.367	3.790	378	0.504	0.305	0.40
20	57.14	1.964	3.685	422	0.461	0.247	0.32
40	78.05	1.252	3.713	FAILS TO CURE			
60	88.89	0.919	2.358				
80	95.52	0.728	2.315				

Catalyst (LT195) = 0.067% w/w

Where [OR] is the concentration of alkoxy groups of crosslinker and [OH] the concentration of hydroxyl groups on the PDMS.

As an alternating approach, the limiting values of Mc obtained from the reported swelling measurement [1] for both the prepolymers used in this study were used for calculation of the r values instead of the quoted molecular weight. This Mc value for each prepolymer has been obtained from the plot of Mc verses percent of crosslinker used for curing. The value of the corresponding prepolymer at the inflection point on the graph, where the Mc value tends to become constant has been used. This value for the long chain prepolymer was 12000 and that for short chain prepolymer was 2250. Basing the calculations on these Mc values, which are understandably the dictating parameter for mechanical properties of polymer networks, the values of r were calculated. These new values show variation from about 4.5 to 0.72, for 3.1 % crosslinker (Table 1), 11 to 1.7 for 9.1 % (Table 2), and about 16 to 2.5 for 12.3 % (Table 3).

Tab. 2. Variation of Tensile Properties of Bimodal Silicone Networks Cured with 9.1 % crosslinker.

P100		r = [OR]/[OH]	$\upsilon \times 10^{19}$	% Eb	UTS (MNm^{-2})	100 % Modulus (MNm^{-2})	E MNm^{-2}
Wt. % P 100	Mole % P 100						
0	0	11.36	6.537	184	0.57	0.46	0.685
4	18.17	8.993	6.532	280	0.71	0.44	0.685
8	31.69	7.445	6.230	304	0.74	0.41	0.681
10	37.21	6.853	6.094	397	0.76	0.40	0.685
14	46.48	5.916	5.564	384	0.79	0.41	0.685
20	57.14	4.909	6.046	423	0.82	0.41	0.579
40	78.05	3.130	4.244	458	0.90	0.34	0.428
60	88.89	2.298	4.767	306	0.55	0.30	0.357
80	95.52	1.719	4.654		FAILS TO CURE		

Catalyst (LT195) = 0.067% w/w

The [OR] and [OH] has the same meaning as that for the previous figure.

In the light of these values based on Mc, the last bimodal compositions cured with 3.1% and that with 9.1 % crosslinker correspond to r value of around 1.7. Below this ratio the composition does not cure. It seems that the calculations based on the experimentally measured Mc are more realistic and closer to stochiometry of the crosslinking of the prepolymers composition as compared to the one when the manufacturer's quoted molecular weights are used for calculations. It is interesting to note from Table 1-3 that the optimum positive effect of bimodality on the tensile properties such as % Eb, UTS, and 100 % modulus are achieved for all the three series when the values of r decreases to about 1.5 - 4. The 1.5 to 4 time greater than stochiometric amount of crosslinker needed for curing of hydroxyfunctional polydimethylsiloxane is not totally new. In fact 1.7 times greater amount of crosslinker has previously been reported by Takeuchi and Cohen [17] for curing of monomodal hydroxyterminated polydimethylsiloxane. They have studied the monomodal polymer network formation and its resulting properties from dihydroxyterminated polydimethylsiloxane through crosslinking with tetraorthosilicate with variation of the ratio of ethoxy group to hydroxyl group, r from 0.9 to 16.7 in presence of stanous 2-ethylhexanoate as a catalyst. It is interesting that they have obtained polymer network having optimum properties with r (ratio of crosslinker functions to chain ends) = 1.7 which is also greater than that required by the stochiometry of the reaction.

Tab. 3. Variation of Tensile Properties of Bimodal Silicone Networks Cured with 12.3 % crosslinker.

P100							
Wt. % P 100	Mole % P 100	r = [OR]/[OH]	$\upsilon \times 10^{19}$	% Eb	UTS (MNm^{-2})	100 % Modulus (MNm^{-2})	E MNm^{-2}
0	0	15.9	7.210	234	0.678	0.459	0.719
4	18.17	12.59	7.395	309	0.80	0.465	0.719
8	31.69	10.422	7.527	384	1.00	0.471	0.719
10	37.21	9.593	7.568	400	1.05	0.490	0.719
14	46.48	8.283	7.822	410	1.148	0.505	0.720
20	57.14	6.872	7.418	441	1.488	0.540	0.760
40	78.05	4.380	6.139	484	1.449	0.489	0.750
60	88.89	3.217	5.564	282	0.828	0.432	0.596
80	95.52	2.547	5.346	124	0.378	0.353	0.398

Catalyst (LT195) = 0.067% w/w
The [OR] and [OH] has the same meaning as that for the previous figure.

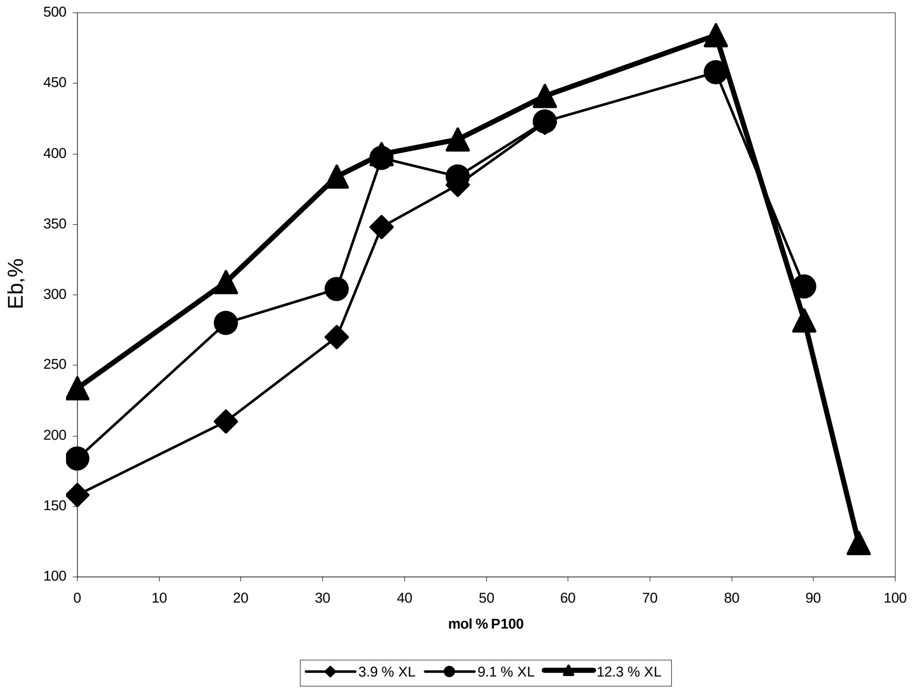

Fig.1. Effect of Bimodality on % Eb of Silicone Networks.

Tensile strength is one of the special characteristics among the widely used mechanical properties. The stress-strain curve of five specimens of each of the silicone composition tested was used for the measurement of mechanical properties information such as % Eb, UTS, 100% modulus and modulus of elasticity. The average of the three modal values for each of the bimodal composition has been presented in graphical forms (Figure 1-4).

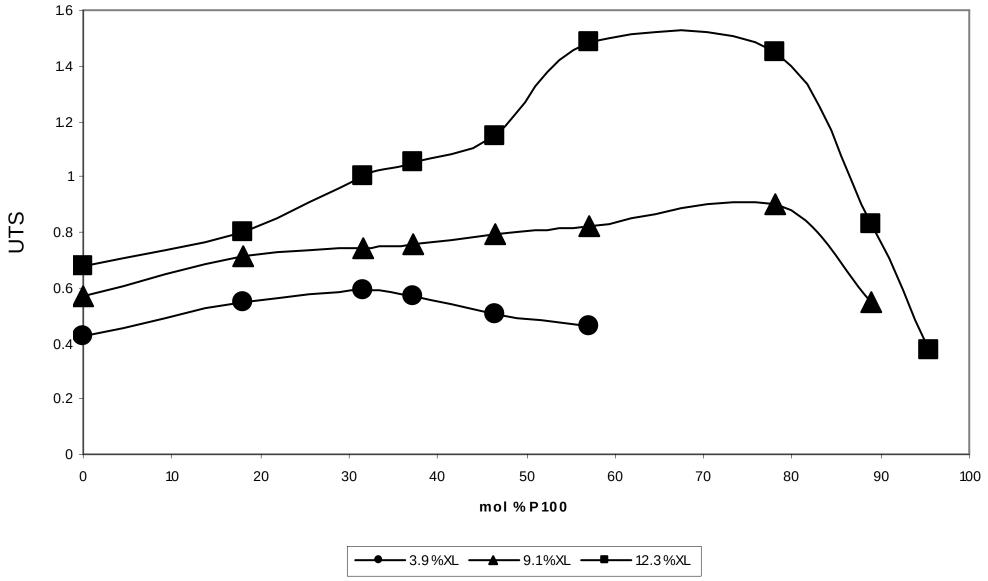

Fig. 2. Effect of Bimodality on UTS of Silicone Networks.

The standard deviation for these measurements varied from 0.05 to 0.09. For bimodal networks prepared by mixing C50 with P100, the %Eb, UTS and 100% modulus generally showed first an increase and then a decrease with increase in concentration of short chain prepolymer (P100). The excessive amount of crosslinker used to cure the mixture has also been found to have a positive effect on most of these properties. The beneficial effect of using these excessive amount of crosslinker for curing, manifest itself (Figure 1-4) even in the absence of bimodality i.e. monomodal network for all the tensile properties i.e. %Eb, UTS, 100 % modulus and elastic modulus. The reason for using an excess of the crosslinker for the series of bimodal networks was first to completely cure the whole series of bimodal mixtures and then to study its effect on the mechanical properties of the polymer networks which has not previously been investigated.

It is clear from Figure 1 that the difference in % Eb for monomodal networks in reference to the concentration of crosslinker used for curing is more prominent i.e. the higher concentration results in higher value of %Eb. However as the bimodality increases, the difference in %Eb decreases until such time that at 70 mole % P100 and onward there is no differentiation between this properties. The %Eb also show increase for all the three concentration of crosslinker used with the increase in concentration of short chains prepolymer P100 up to about 70 mol %. This increase in % Eb follows almost a linear proportionality with mol % P100 for all the three concentration of crosslinker used. The increase in %Eb of the silicone networks due to bimodality has been found to be 2.1 to almost 2.7 times that of the monomodal networks cured with all the three (starting from low to high) concentrations of crosslinker up to about 70-mol % of P100 concentration. However, above 70-mol % P100, a decrease in % Eb is observed for the silicone network cure with 9.1 % as well as for the 12.3 % crosslinker. Surprisingly, there is not much difference in the values of %Eb for the bimodal composition cured with different amount of crosslinker. In the case of polymer networks cured with 3.9 % crosslinker, these materials fails to cure when concentration of short chain prepolymer increases above the range of 57.14 mole %, and so the mechanical properties cannot be measured.

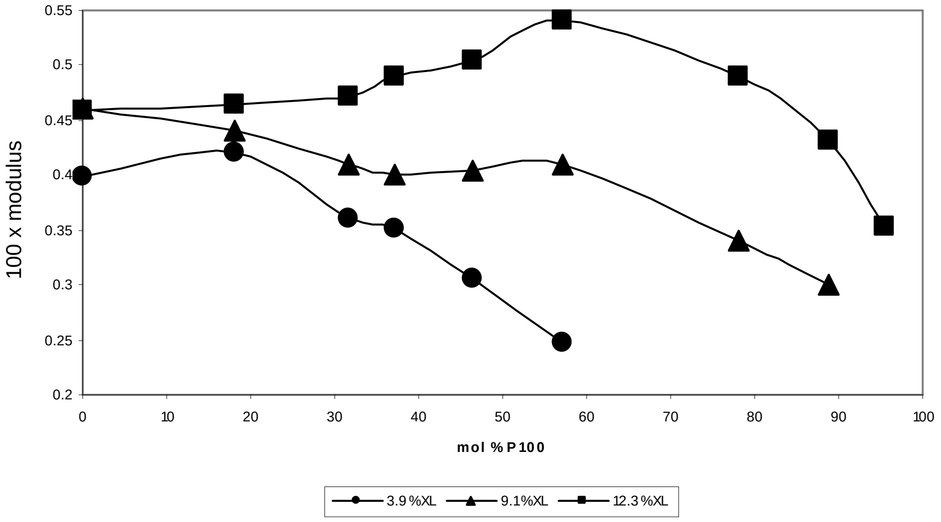

Fig. 3. Effect of Bimodality on 100 % modulus of Silicone Networks.

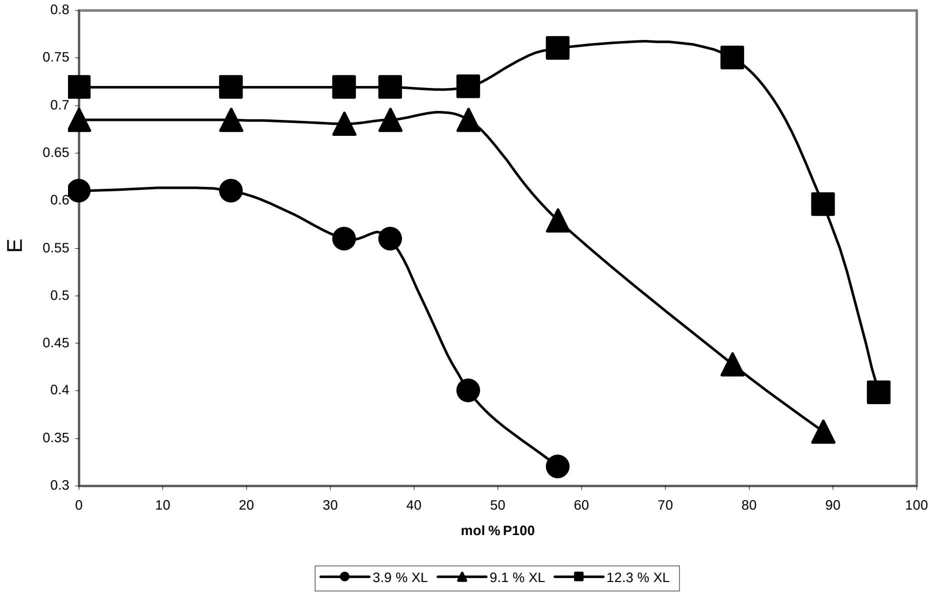

Fig. 4. Effect of Bimodality on Elastic Modulus (E) of Silicone Networks.

In the case of UTS, again the concentration of crosllinker has positive effect both on monomodal as well as bimodal silicone networks. A higher increase in UTS with the increase in bimodality i.e. increases in concentration of P100 can be seen for the bimodal network cured with higher content of crosslinker (Figure 2**).** In other cases where the mixture was cured with low amount of crosslinker, this effect is a very minor one. The increase in the UTS is dependent upon not only on the short chain prepolymers concentration but also the concentration of crosslinker used. The dependency of tensile properties of silicone polymer networks on bimodality as well as the concentration of crosslinker is new in its own capacity. However, a similar dependency for the tear property of unfilled [1] and 17.2 % filled [2] silicone networks has previously been reported and discussed by the same author in great details. As shown in Figure 2, the materials cured with 12.3 % crosslinker increases the UTS as high as up to 2 times that of the materials made with monomodal prepolymer with the increased bimodality. In the case of networks prepared with 3.9% crosslinker the increase in properties was slight and a maximum was observed at about 35-mole % short chain prepolymer. A comparison of tensile strength of unfilled bimodal networks with that of the corresponding tear properties published earlier [1, 2] shows that the overall improvement i.e. 2 fold in tensile property compared to that of 2.5 fold increase in tear energy for unfilled and 3.5 times for 17.2 % w/w pyrogenic silica filled silicone is less. The less pronounced overall improvement in tensile results due to bimodality may be attributed to the nature of the test i.e. tensile testing probe bulk properties and so is influenced more by superficial defects such as flaws, bubbles etc. On the other hand, the tear energy represents the intrinsic nature of the materials and hence the values are comparatively dictated more by the molecular nature of the concerned polymer and less affected by the superficial defects. It is interesting that the highest point in the UTS is observed at about 30 mol % P100 for the low concentration of crosslinker used for curing but in case of the materials cured with higher concentration of crosslinker, the hump shifted to about 70 mol % P100. The property of 100 % modulus shows no significant increase in the values with the increase in mole % P100 (Figure-3).

As obvious from Figures 3 and 4, the 100 % modulus and elastic modulus (E) of the silicone polymer networks do not follow the same trend as shown by that of %Eb and UTS. The values of 100% modulus and that of E remain constant during the first stage of increase in concentration of P100 and then decrease for all the materials cured with all the three different concentration of crosslinker. It shows that the bimodality does not have any positive effect on the 100% modulus and elastic modulus as compared to the other tensile properties where enhancement in the concerned behaviours is observed. It is interesting that in contrast to the %Eb, the UTS, 100 % modulus and elastic modulus show greater difference in magnitude for different concentration of crosslinker used for curing in the limit of higher bimodality instead of lower bimodality range.

A plausible explanation for this contrast is that %Eb in silicone network is more dictated by the larger chain length where as the rest of the tensile properties i.e. the UTS, 100% modulus and elastic modulus are characteristics of the hardness of the polymer network and hence dictated by the shorter chains. When the monomodal silicone network is subjected to %Eb, the concentration of crosslinker has pronounced differentiating effect on this property. However as the proportion of the longer chain prepolymer is decreased in the bimodal mixture through incorporation of shorter chain prepolymer, the differentiation in magnitude of the %Eb for different amount of crosslinker used for curing continuously decreases until at 70 mol % P100, it almost disappears.

In the case of the UTS, 100 % modulus and elastic modulus, the properties are represented by the short chain length prepolymer within the network and hence the differentiation in magnitude in reference to the amount of crosslinker used for curing is observed at higher concentration of short chain HOPDMS.

As far as the mechanical properties are concerned, the primary variable in any crosslinked rubber for controlling the mechanical properties is the degree of crosslinking which is defined as the number of network chains per unit volume (ν). Mathematically it is equated with other parameter as

$$\nu = \rho N/Mc \tag{1}$$

Where ρ represents density of the polymer network, N is is the Avogadro number and Mc is the average molecular weight between crosslinks. The above equation has been used for calculation of the υ values and these are presented in Table 1-3. The values of Mc for the above equation were used from the equilibrium swelling measurement method reported in the previous publication [1], and hence the above equation gives exclusively the number of effective (bound from both ends) polymer network chains per unit volume rather than that having some contribution from the ineffective (dangling) chains as in the case of using elastic property measurements. In order to see whether the enhanced mechanical properties in bimodal polymer networks can be reflected in terms of variation in the degree of crosslinking (υ), the value of υ for all the three series of bimodal networks (presented in Table 1-3) have been plotted against the mole % P100 as Figure 5.

Figure 5 show that it has two distinct portions. In the first portion for each series, the value of υ for each series of bimodal networks cured with different amount of crosslinkers suggests no appreciable change. The insignificance change in the value of υ with increase in concentration of short chain prepolymer suggests that the increase in mechanical properties cannot be explained for bimodal networks on the basis of variation in the degree of crosslinking. In the second portion, there is an obvious decrease in the values of υ with variation of short chain prepolymer. As for the last values in each series showing a decreased trend; these represents the polymer network which fail to fully cure (Table 1-3) and so can be rejected.

In order to explain the anomalous behaviour of enhancement in tensile properties of silicone polymer network due to bimodality, the concept of phase transition in polymer blend can also be applied here. The blend of HOPDMS prepolymer, as the name shows, comprises of two prepolymer of the same nature. That is why its components are much more miscible with one another as compared to the other type of blends where the two components are of different nature and hence bimodal prepolymer mixtures can be considered as a truly miscible one-phase blend. Generally, the present bimodal networks show optimum in tensile properties at around 70 mol % P100 which corresponds to 0.5 volume fraction of P100. Usually in polymer blends this is the point where phase inversion start to takes place. Phase inversion occurs when the minority component in the blend becomes continuous phase and the majority component becomes the dispersed one [18]. The phenomenon of phase inversion normally depends on the blend composition and the viscosities of the polymer components [19-24].

Initially the long chain prepolymer i.e. C50 is in majority and forms a continuous phase in the bimodal mixture. As the bimodality increases, the introduction of short chain prepolymer somehow properly fit with the long chain prepolymer in the resulting polymer networks and enhances the tensile properties. This phenomenon optimises at around 70 mol % (or 0.5 volume fraction) P100, where a co-continuous morphology in the bimodal polymer network results in the best properties in each series. It seems that phase inversion or phase transition start to take place at around 70 mole % P100 in bimodal networks where an interpenetrating network like structure is formed that exhibit maxima in tensile properties such as %Eb and UTS. This behaviour is similar to the one reported for two component blend of Polypropylene (PP)/Ethylene propylene-diene monomer (EPDMS) [25, 26]

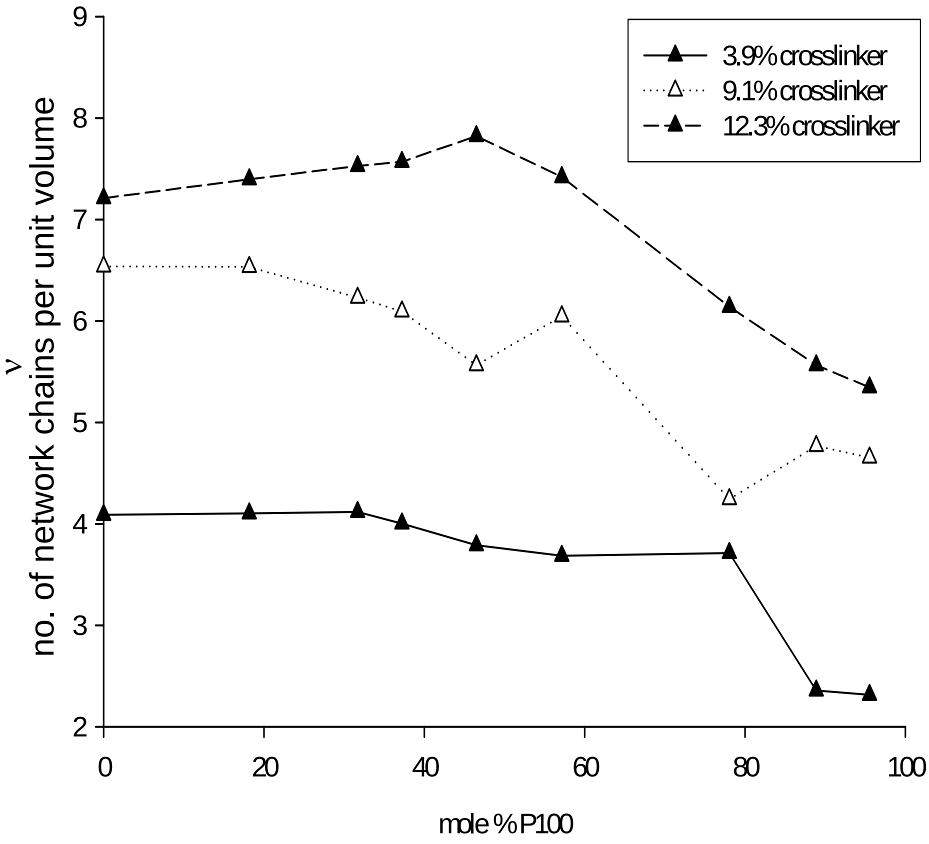

Fig. 5. Effect of concentration of crosslinker and P100 on the number of network chains per unit volume.

The exhibition of magnitude of this maxima with bimodality at around 70 mol % (0.5 volume fraction) P100 has been observed to decrease in the order i.e. %Eb > UTS > 100 % modulus > Elastic modulus. The lack of indication of phase transition and hence the obscurity of information about the structure or interaction in the case of modulus has also previously been reported [27] for the blend of PP/Polyvinyl chloride (PVC). However in the present case of bimodality studies, there is an indication of this phase transition but not as much clear as in the case of %Eb and UTS.

The enhancement in tensile properties due to bimodality has been found to be in accordance with the pattern reported by previous researchers for tear property [28, 29]. The concept of limited chain extensibility arising from a bimodal molecular weight distribution provides a qualitatively satisfying explanation for the improvement in physical properties such as UTS, %Eb and tear properties. The increase in tensile properties observed for bimodal networks (Figures 1-3) cured with very high concentrations of crosslinker seem to be due to the role of trifucntional crosslinker as a reinforcing agent by condensing with it. This reinforcement is further significantly accentuated by the established effect of bimodality. The polymer networks prepared by using high concentration of crosslinker shows higher %Eb, UTS etc. compared with those cured with low concentration of crosslinker. Like the tear property, tensile behaviour of the networks is sensitive to the concentration of crosslinker and generally follows the same trend.

The excess amount of crosslinker does complicate the concerned chemical reaction. Apart from the normal crosslinking of the HOPDMS in this particular case, the excess amount of crosslinker increases the chances of crosslinker molecules to react with one another and at the same time in some instances due to steric hindrance act as chain extender between HOPDMS molecules. However unfortunately the role and the extent of each of these side reactions in the overall crosslinking cannot be separated and measured quantitatively in the present conditions. As far as the role of catalyst during crosslinking of silicone prepolymer is concerned, its presence has been found and reported [30,31] to be essential for curing within a specified time. However, its concentration did not have wide-ranging effects on the physical properties of the resulting polymer networks.

In spite of the fact that a good deal of work has been carried out to study the bimodal networks, the reported mechanisms of enhancement in mechanical properties due to bimodality are still not clear and different opinions have been reported by different researchers. For example Llorenete et al [11] and Lin-Xi et al [32] think that in bimodal networks stress during testing is transferred to the easily deformable chains. Herbert et al [33] believe more tie chains and entanglements to be responsible for the enhancement in mechanical properties of bimodal networks. Bahar et al [34] concluded that segmental orientation in the long chain of bimodal network during deformation is longer than the unimodal network. Whichever combination of the factors is involved, the fact is that in addition to the previously published reports, that mechanical properties are acutely dependent upon the degree of crosslinking and primary molecular weight [35, 36]; bimodality is now also being considered as playing a significant role in enhancing mechanical properties in the unfilled silicone polymer network formation.

In conclusion, the effect of bimodality and the amount of crosslinker on the tensile properties of silicone networks was found to be in general beneficial. Interestingly, the excessive amount of crosslinker used for curing some how provide additional reinforcement to the silicone network. This reinforcement is further significantly accentuated by the established effect of bimodality. The %Eb of the silicone networks increased to almost 2.1 to 3 times that of monomodal network for the networks cured with all the three concentration of crosslinker (3.9, 9.1 and 12.3%). The optimum property was observed at about 70 mol % of P100 concentration. However the UTS showed somewhat relatively lower enhancement i.e. 2 fold increase with the increase in concentration of crosslinker for the same compositions. For 100% modulus, the enhancement is further lower in magnitude and for that of the elastic modulus of the materials; the bimodality has no effect on this property. In this respect, the order of sensitivity of these tested tensile properties to the effect of bimodality at about 70 mol % of short chain prepolymer can be concluded as: %Eb > UTS > 100% modulus > elastic modulus. It has been established for the first time that in addition to the previously published reports, the tensile strength is acutely dependent not only upon the degree of crosslinking and primary molecular weight; but also bimodality and the amount of crosslinker concentration for preparation in silicone polymer networks. The concept of phase inversion (or phase transition) used in polymer blends has for the first time been applied to the bimodal polymer networks and it has been shown that maxima in tensile properties generally corresponds to phase inversion which takes place at 0.5 volume fraction of short chain prepolymer i.e. P100 (70 mol %P100) which is in accordance with the literature.

Experimental part

Materials

The liquid hydroxyfunctional polydimethylsiloxanes (HOPDMS) prepolymers (Silopren), long chain (C50, viscosity average M.Wt = 88,000 and polydispersity = 1.9) and a rather low molecular weight (short chain) silicone prepolymer of viscosity 100 mPa s (P 100, viscosity average M. Wt 3500 and polydispersity = 1.75) used were supplied by Bayer Ltd. and Petrarch Ltd. respectively. The catalyst, dioctyltinmaleate (DOTM) (LT195, M.W 459), was supplied by Lankro Ltd. and the crosslinker vinyltris (ethoxymethoxy) silane VTEMS (A172, M.W 280.4) by Union Carbide Ltd.

Methods

Mixing the short with long chain HOPDMS prepolymers was carried out to make a number of bimodal mixtures. The content of short chain HOPDMS was systematically varied in the range 0-80% w/w (0/50 to 40/10 w/w) making the total weight equal to 50g. A constant amount (0.04% w/w) of catalyst DOCTM was used for curing of each of the composition. Three different weights of crosslinker 2 g (3.9%), 5 g (9.1%) and 7 g (12.3%) were used for the above series of bimodal mixtures. These compositions were cast onto separate polyethylene plates and spread to a uniform film of approximately 1.4 mm in thickness. The films were left for seven days at room temperature i.e. 23 ^{0}C in an open air to complete the crosslinking reaction.

Dumbbell shaped specimens were cut from the films according to BS 903 Part A2 1956. Die C. Instran Model 4301 High Wycombe (England) was used for measurement of tensile properties i.e. ultimate tensile strength (UTS) and percent elongation at break (% Eb) at a strain rate of 50 mm/min. An average of the three modal values out of five specimens tested has been used for presentation.

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