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Designing Heterogeneity into Bimodal Elastomeric PDMS Networks

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SUMMARY: Bimodal poly(dimethylsiloxane) (PDMS) networks prepared using a dual-step process have been studied. It is shown that these networks exhibit a significant increase in equilibrium modulus. This reinforcement can be obtained by adjusting a process parameter, the "heterogeneity time", during network preparation. The increase in modulus is attributed to the clustering of the short chains that is effected through proper use of heterogeneity time.

Introduction

The concept of bimodal networks has clearly shown the importance of spatial heterogeneity on physical properties, such as modulus. Typically, bimodal networks result from blending difunctional long and short chains and cross-linking them together. The unexpected mechanical properties exhibited by these networks have been attributed to the limited extensibility of the short chains.[1-3] A conceptualization of a typical bimodal network is shown in Fig. 1.

Fig. 1: Schematic of a typical bimodal network. Bold lines denote short chains.

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Conventional, single-step bimodal networks (SSBN) as shown in Fig. 1 are prepared, as the term implies, by a single-step process that involves pre-determined amounts of short chains, long chains and stoichiometric amounts of crosslinker in the presence of a catalyst. However, a two step method could also be used.[4-7)] This involves pre-reacting, for a specific amount of time (heterogeneity time), a certain amount of short chains with stoichiometric amounts of cross-linking agent. The long chains are then mixed with stoichiometric amount of cross-linking agent and added to the short chain mixture. This results in networks of structure as shown in Fig. 2.

Fig. 2: Schematic of a bimodal network of enhanced spatial heterogeneity.

These networks have clusters of small chains that result in enhanced spatial heterogeneity. We term these networks dual-step bimodal networks (DSBN).

Experimental Part

Hydroxyl terminated PDMS chains of number average molar mass (M_n) 17,800 $g{\cdot}mol^{-1}$ and 780 $g{\cdot}mol^{-1}$ were employed in all the experiments described here. The cross-linking agent employed was tetraethoxysilane. The catalyst was tin octoate in 50% PDMS solution. All of the chemicals were obtained from Huels America. Molar masses were determined using GPC (Gel Permeation Chromatography; Waters Associates) and VPO (Vapor Phase Osmometer; Knauer).

Pre-determined amounts of short chains were mixed with stoichiometric amount of cross-linking agent and 0.5 wt% active catalyst. The mixture was allowed to pre-react for a desired heterogeneity time under nitrogen. Long chains were separately mixed with stoichiometric amounts of crosslinking agent and 0.5 wt% catalyst. Just before the elapse of the heterogeneity time the long chains were added to the short chains, the contents mixed thoroughly, and poured into polycarbonate molds. The compositions of the networks prepared are as shown in Table 1.

Table 1: Matrix of compositions for DSBN networks for this work.

$Mnl = 17.800\ g\cdot mol^{-1}$
$MnS = 780\ g\cdot mol^{-1}$

80 mol% bimodal	→	T = 0 hour	T = 3 hour	T = 5 hour
85 mol% bimodal	→	T = 0 hour	T = 3 hour	T = 5 hour
90 mol% bimodal	T = 0 hour	T = 1 hour	T = 2 hour	T = 3 hour
92 mol% bimodal	T = 0 hour	T = 1 hour	T = 2 hour	T = 3 hour
94 mol% bimodal	T = 0 hour	T = 1 hour	T = 2 hour	T = 3 hour

Heterogeneity times varied between 1 and 5 hours. The networks were then allowed to cure for an additional two days under nitrogen atmosphere. They were then removed from the mold and pre-weighed portions of the networks were swollen in toluene for three days and then successively de-swollen in methanol to extract the sol from these networks. Typical sol fractions for acceptable networks were around 3-5 wt%.

A mini tensile testing machine was used to strain the sample. The output of the load cell can be read from either a chart recorder or a digital readout. The equilibrium modulus $[f^*]$ is defined as:

$$[f^*] = f^*/(\alpha^2 - 1/\alpha) \qquad (1)$$

where $f^* = (f/A^*)$ is the true stress (N·mm^{-2}). All experiments were done until maximum extensibility was reached. All samples were tested for reversibility during testing. Torques were determined by a Haake viscometer.

Results and Discussion

As the clustering of small chains brings about heterogeneity, it is necessary to determine the length of time necessary to form clusters. A Haake viscometer was used to monitor the increase of viscosity over time. From this variation of torque as a function of time (Fig. 3) it can be seen that it takes approximately 10-11 hours for the chains to cross-link at a catalyst concentration of 1.0 wt% and about 2-3 hours at a catalyst concentration of 2.0 wt%.

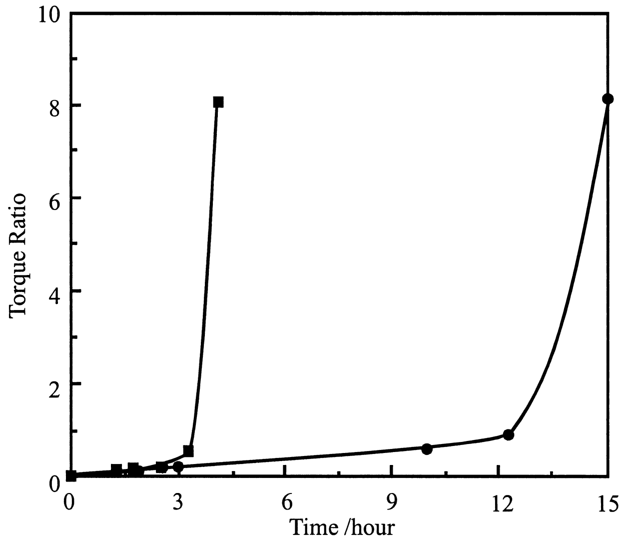

Fig. 3: Torque ratios for short chain blends at two catalyst levels. Circles denote 1 wt% and squares 2 wt% concentration.

It is critical to add the long-chains blend to the short-chains blend before the latter reaches macroscopic gelation to avoid macroscopic phase separation. Since the catalyst concentration used to prepare networks was less than 1%, a decision to use a series of heterogeneity times less than 10 hours was made. However it was observed that networks with heterogeneity times greater than 6 hours had an unacceptably high sol fraction (>10 wt%) and therefore heterogeneity times of shorter than 6 hours were used.

Fig. 4 shows the variation of the number average molar mass with the heterogeneity time. It can be seen that the number average molecular weight shows a significant increase with time. It is concluded that at this low catalyst concentration (0.5 wt%), the increase in molecular weight must be due to the clustering of the small chains.

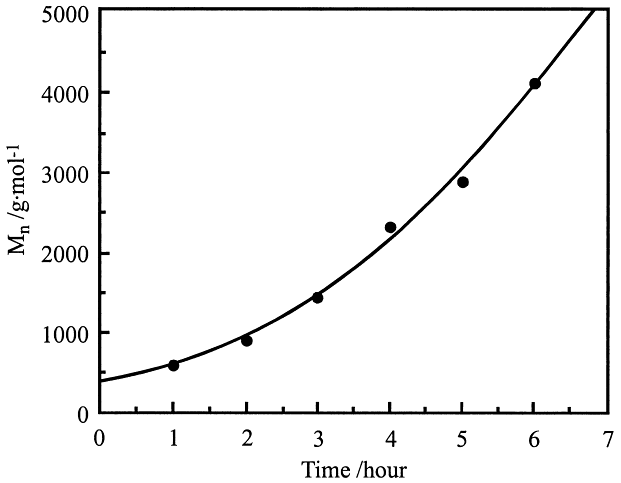

Fig. 4: Number-average molar mass of pre-reacted short chain clusters as a function of heterogeneity time.

The variation of molar mass between crosslinks as a function of heterogeneity time is shown in Fig. 5. It can be seen that the crosslink density of these networks shows an increase with heterogeneity time, thus supporting the notion of small-chain cluster creation.

The effect of enhanced heterogeneity is expected to show up in the physical properties of these networks. Fig. 6 shows the Mooney-Rivlin representation for a 90 mol% DSBN. Equilibrium modulus values show a consistent increase with heterogeneity time, throughout the elongation range. This increase is attributed to the increased size of the short-chain clusters, which act as giant cross-links of multiple functionality. Comparison to a SSBN of similar composition shows that the increase in modulus is about 25%.

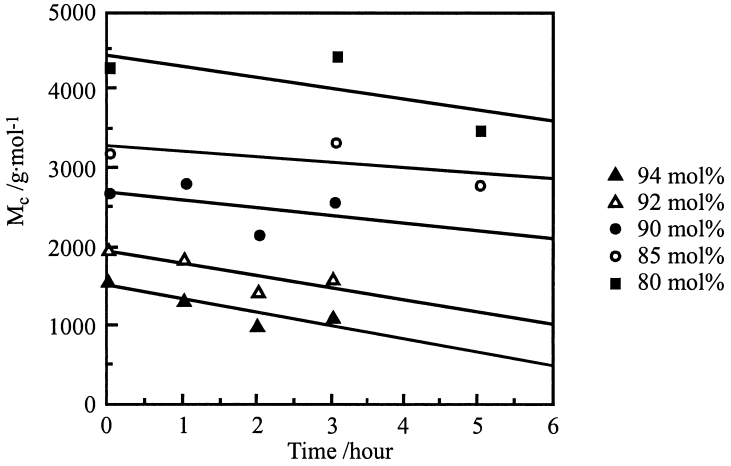

Fig. 5: Variation of molecular weight between cross-links as a function of heterogeneity time. Symbols denote the respective mol% of short chains.

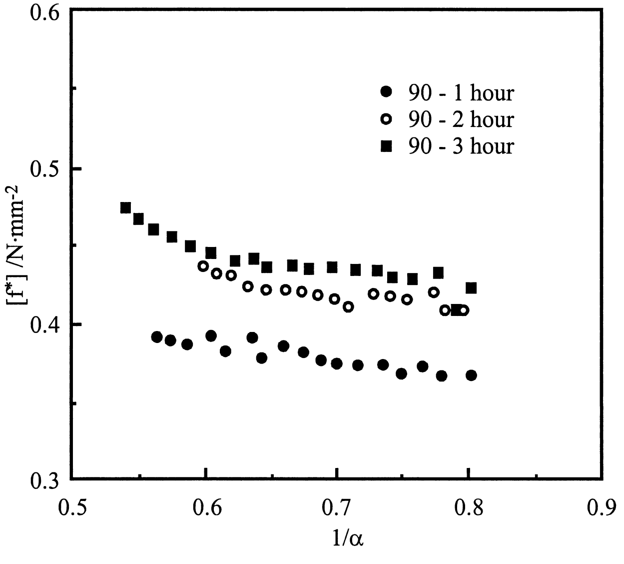

Fig. 6: Mooney-Rivlin plot of a 90 mol% DSBN at three heterogeneity times.

Fig. 7 shows the variation of modulus as a function of heterogeneity time for a 92 mol% DSBN. Modulus values are even higher, around 30%, over a SSBN of similar composition. As expected, longer heterogeneity times yield tougher networks. This reinforcement is attributed to the combination of multifunctional short chain clusters and their higher concentration in this network.

DSBNs containing short chain concentration greater than 92 mol% show a much lesser increase in modulus than the networks containing 90 and 92 mol% short chains. This may be because SSBNs containing short chains greater than 92 mol% are inherently heterogeneous and using a dual step process does not apparently increase the heterogeneity considerably. This observation is in line with similar observations on other bimodal networks.[7)] It is concluded that only DSBNs prepared within a concentration range of short chains will yield materials with considerable reinforcement.

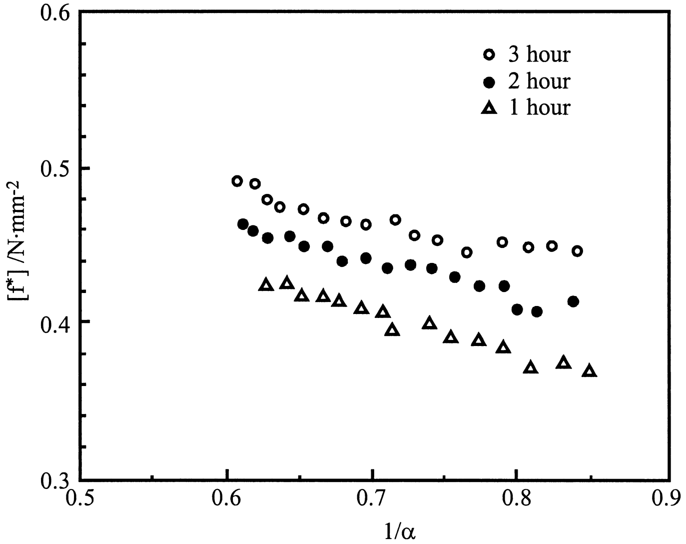

Fig. 7: Mooney-Rivlin plot for a 92 mol% DSBN at three heterogeneity times.

Conclusions

DSBNs of short chain concentrations ranging from 80 mol% to 94 mol% and with heterogeneity times ranging from 1-5 hours were prepared. Of those only DSBNs containing short-chain concentrations in the range of 85-92 mol% showed substantial increase in modulus when compared to SSBNs of similar compositions. The increase in modulus is not as pronounced as the concentration of short chains becomes greater than 94 mol%. Heterogeneity times greater than 5 hours resulted in networks with defects, as this was determined from their high sol fractions. There also appears to be a composition range dependent on the concentration of the short chains where maximum improvement in modulus can be obtained. It is worth noticing that reinforcement is achieved in the absence of any particulate fillers.

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