

The Effect of Bimodality on the Tear Properties of Filled Silicone Networks

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ABSTRACT: The effect of blending a short and a long chain silicone prepolymer, that is, the effect of bimodality on tear properties of filled polymer networks has been investigated. Two concentrations, namely, 17.2 and 30.2% w/w of the filler (HDK) were used. The contents of short chain prepolymers have been varied from 0 to 69% w/w and 0 to 58% w/w for 17.2 and 30.2% filled polymer, respectively. The concentration of crosslinker and catalyst added were kept constant, namely, 13.79 and 0.07%, respectively, for each composition. It has been shown that up to a threshold concentration of filler and short chain prepolymers, the application of bimodality has beneficial effects of increasing

tear energy up to 3.5 times that of the tear energy of the concerned filled monomodal polymer network. Above this threshold limit, further increase in concentration of filler or short chain prepolymers, contrary to expectation, adversely affected the tear properties of the filled polymer networks. In light of the results obtained, the mechanism of enhancement in the tear properties of the polymer network due to bimodality in the filled polymer system has been discussed. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1719–1722, 2004

Key words: bimodal polymer networks; crosslinking; enhancement; monomodal polymer networks; tear energy

INTRODUCTION

The blending of long and short chains of the same polymer gives a broader, bimodal molecular weight distribution; and a network prepared from such a blend is known as a bimodal network. The practical significance of such a polymer network is that it possess a combination of good mechanical properties, such as tear energy, tensile behavior, and resilience.^{1,2} The improvement in these properties originates by creating locally high crosslink density between relatively long chain polymers in a network by blending a small proportion of short chain prepolymers with long chain prepolymers prior to vulcanization. The accepted view is that the low incidence of chain irregularities (i.e., the presence of polymer ends that do not form part of the load bearing networks) and the non-Gaussian effect are responsible for the enhancement. This non-Gaussian effect is believed to arise from the limited extensibility of the short chain prepolymers component and are responsible for the improvement in mechanical properties.^{3,4} The short chain prepolymers within the bimodal networks creates domains of crosslink density that support the applied stress, thus hiding the imperfections that are more exposed in monomodal networks. The longer prepolymer chains,

on the other hand, provide a high tear energy, in accordance with the Lake–Thomas equation.⁵ These effects, coupled together, make bimodal polymer networks superior to monomodal ones in respect of tear properties. Improvement in tensile and shear properties due to bimodality has also been observed for unfilled silicone networks.^{6,7} A great deal of work has been done by other researchers^{8–14} to prepare such tough elastomers by using this simple technique. Improvement in mechanical properties due to bimodality is not only associated with silicone networks but has also been reported for polyisoprene.¹⁵ Grobler and McGill observed improvement in tear and tensile properties for polyisoprene via different curing conditions and attributed this to network heterogeneity.

The properties of these bimodal networks cannot be explained in terms of the existing theories of rubber elasticity or the Lake–Thomas theory.⁵ Yanyo and Kelley¹⁴ claim to predict the improvement in mechanical properties of the unfilled bimodal network with a modified version of the Lake–Thomas equation. In our previous study,¹ about an investigation of the tear energy of the bimodal silicone networks cured with different concentration of crosslinker, it has been shown that even the Yanyo–Kelley equation does not fully predict the enhancement in the properties of polymer networks by introducing bimodality into them. Whatever the status of explanation of the enhancement due to bimodality in the properties of the polymeric network is, these properties are desirable.

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The anomalous behaviors of improved mechanical properties of bimodal networks are reported only for unfilled polymer networks. It is an established fact that fillers are used as a reinforcing agents in various polymer systems. Naturally, interest is aroused to study and achieve further enhancement, if any, in mechanical properties of the filled polymer network by virtue of bimodality.

In the present work, the effect of bimodality on tear properties of bimodal silicone networks in the presence of pyrogenic silica HDK type 2000–4 as a filler, which is also a reinforcing agent for polymeric systems, has been studied. In this respect two concentrations, namely, 17.2 and 30.2% w/w HDK, in conjunction with a wide range of concentration of short chain silicone prepolymers, have been used for silicone network preparation, and then these networks have been studied for their tear property.

EXPERIMENTAL

Materials

The liquid hydroxyfunctional polydimethylsiloxanes (HOPDMS) prepolymers (Silopren), long chain (C50, M.Wt = 88,000), and a rather low molecular weight (short chain) silicone prepolymer of viscosity 100 mPa s (P 100) 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. The filler employed was pyrogenic silica HDK type H 2000–4 supplied by Wacker Ltd.

The compositions having two concentrations, namely, 17.2 and 30.2% w/w of the filler HDK based on the total weight, were used with C50 separately. The amount of short chain prepolymer (P100) was varied from 0 to 69% and 0 to 58% for the 17.2 and 30.2% filled HOPDMS, respectively. The concentration of crosslinker and catalyst added were kept constant, that is, 13.79 and 0.7% respectively, for each composition. Each of the compositions, after mixing to a homogeneous paste, was cast onto a polyethylene plate separately and spread to a uniform film of approximately 1.4 mm thickness. These films were left in the open air at room temperature (25°C) for seven days to complete the crosslinking (curing) reaction.

Tear property measurements

The specimens for tear test from each composition were prepared from a trousers cutter according to BS 6899: 1976. At least three specimens were chosen for each composition. A Monsanto 500 rubber testing machine was used for measuring the tear properties. The tests were carried out at a strain rate of 50 mm/min,

and the corresponding tear curves were obtained from the chart recorder connected to the rubber testing machine. Thin strips of polyethylene terephthalate films were stapled to both legs of the specimens to avoid stretching during the test. The tear energy (T) can be calculated from the following equation¹⁶:

$$T = 2\lambda F/h - 2aW \quad (1)$$

where λ is the extension ratio in the legs, F is the force required to propagate the tear at a given temperature, h the torn thickness, 2a the width of the test piece, and W the elastic energy stored in the sample. Preventing the sample from stretching ($\lambda = 1$) and so maintaining the elastic energy (W) at zero simplifies the above equation to

$$T = 2F/h \quad (2)$$

This equation was used for calculation of tear energies of all the polymer network compositions.

RESULTS AND DISCUSSION

The concept of bimodality and its expected result in the enhancement of tear properties has been tested for two filled (17.2 and 30.2% HDK) in C50 compositions with varying amount of P100. The mole % of P100 was calculated on the basis of weight of C50 and P100 used, and their respective molecular weights between junctions (Mc) values. The amount of filler along with the catalyst was ignored because taking these into account complicates the calculations (due to uncertainty of OH groups on the filler) and suppresses the concentration of P100 so that the graphical presentation becomes less prominent. This point has already been elaborated on previously¹ in connection with the work on the effect of bimodality on tear properties of unfilled silicone networks.

The tear energy for the 17.2% filled system increased with increase in concentration of P100 up to about 95 mol (64% w/w) P100 and then dropped. The data is depicted in Figure 1. It is noticeable that the maximum tear energy achieved is about 3.5 times higher than that of energy of the concerned monomodal filled network. In the case of the heavily loaded (30.2% HDK) system, the effect of bimodality is reversed, that is, the increase in concentration of P100 decreased the tear energy of the bimodal silicone networks (Fig. 1).

The application of bimodality in polymer networks for the improvement of their mechanical properties, such as tensile and elongation behavior, is established and has been reported^{17–24} by a large number of researchers. A number of explanations and theories have been put forward to describe the mechanism of improvement in the properties due to bimodality.

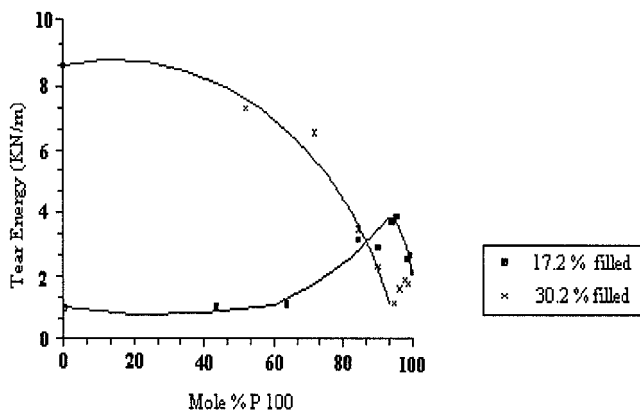


Figure 1 Trousers tear energy of filled silicone networks with concentration of P100.

It is an interesting fact that bimodal networks exhibit high ultimate strength without the usual decrease in maximum extensibility. To explain the enhancement in the tensile properties of silicone bimodal networks, some researchers^{11,25} have partitioned the elongation during deformation nonaffinely between the short chain and long prepolymers. It has been shown that most of the strain is transferred to the longer, more easily deformable chains with which the short chains communicate. It is reported that the energy contribution to elastic force of a bimodal network is less than that of a singular long PDMS network.

Hubert et al.,²⁶ who reported modification of the count distribution within the molecular architecture of bimodal polyethylene polymer with respect to unimodal copolymers, claim that bimodal copolymers have more tie chains and chain entanglements than the corresponding unimodal copolymers. They attributed the better fibrillar strength resulting from these topological changes to the macromolecular network efficiency. They explained that the effect was an increase of chain entanglement and tie chain densities resulting from reduced propensity of long chain with short chain branching to regular chain folding and chain reeling during crystallization.

Bahar et al.²⁷ studied bimodal networks in terms of the state of segmental orientation in uniaxially deformed in comparison to the behavior of corresponding unimodal networks. The results of their formulation showed that segmental orientation in the long chains of the bimodal network is larger than the corresponding in the unimodal network. Conversely, shorter chains orient less in the bimodal network compared to the corresponding chains in the unimodal network. Besbes et al.²⁸ concluded that segmental orientation in bimodal PDMS networks predominantly reflects intramolecular contribution resulting from network topology, the effect of bimodality, the constraints affecting junction fluctuations, and the state of macroscopic strain.

The enhancement in mechanical properties of polymer networks due to bimodality, as reported¹ previously, is believed to arise from the limited extensibility of the short chain prepolymer component present in the polymer network. The hiding of imperfections due to increase in crosslink density with the increase in short chains within the bimodal network as discussed make the bimodal network superior to the monomodal one in terms of tear properties. While incorporation of short chain prepolymers enhanced tear properties, bimodality in the corresponding filled silicone polymer networks does increase the tear properties up to a specific concentration of filler and short chain silicone prepolymer. The low degree of enhancement in the tear property for the 17.2% filled system up to about 95 mol % (64% w/w) presented as Figure 1 might be explained as follows.

The surface silanol groups of the filler are active sites and are well known to be responsible for reinforcing the material, presumably by direct hydrogen bonding to the siloxane backbone of the principal prepolymer. In the case of 17.2% (w/w) filled networks, the OH groups on the filler reacting via crosslinker with C50 are comparatively fewer, and the gradual increase in concentration of short chain prepolymers in to the polymer system probably results in placement of long chain prepolymers (C50) via crosslinker with short chain prepolymers in such a way that the polymer network gradually shifts from monomodal network to bimodal network. This results in bimodal reinforcement of the networks up to the concentration of 95 mol % of P100. At about 95 mol % of P100, the polymer network represents a comparatively ideal bimodal network for the filled system. Further increases in P100 increases the probability of its reaction with the surface silanol groups of the filler in the presence of catalyst and crosslinker, and hence reduces its activity. As a result, a decrease in tear energies is observed.

Increases in concentration of filler above 17.2% w/w leads to inferior tear properties. The distance between filler particles in polymer networks is probably such that surface OH groups interact via H-bonding, possibly forming rigid chains. At this concentration, the additional short chain silicone prepolymer results merely in creation of stress concentration centers where the applied load cannot distribute itself and the network is torn with low tear energy. In the case of the highly loaded (30.2% HDK) system, the OH groups on the filler are more than sufficient to react via crosslinker with the amounts of P100 available and make the filler inactive. The inactive filler may now act as stress concentration centers. In the presence of sufficient filler, the prepolymer chains anchor to it at different points, then the successive increments of P100 decrease the degree of freedom of orientation of polymer chain in the resulting polymer networks.

These stress concentration centers and low degree of orientation of polymer chains result in a decrease in the tear properties. Moreover, it is due to this reaction of P100 with filler that P100 are no longer available for the enhancement which bimodality previously¹ conferred.

CONCLUSION

The incorporation of short chain prepolymers to the long chain prepolymers within the bimodal network is ascribed a major role on the topological changes, the effect of which is reflected in the enhancement of the mechanical properties such as tear energy. The effect of bimodality has promising results in terms of the high tear energy of the networks. The 2.5 fold increase in trousers tear energy compared with the monomodal network has already been reported¹ at 95 mol % concentration of P100. However, the application of bimodality to the filled system has enhancing effect (3.5 times that of the concerned monomodal filled polymer networks) on the tear energy up to a threshold limit of the concentration of filler and short chain prepolymer. Above that concentration limit, increase in concentration of short chain prepolymer or that of filler adversely affects the tear energy of the filled silicone polymer network.

It is concluded that the enhancement in tear properties due to bimodality is actually controlled with the overall number of OH groups in the system, that is, on short chain, long chain, and filler. Once a threshold limit is reached in this respect, there is no beneficial effect on the tear properties of the present polymer network and, in fact, this property shows a drastic decrease by increasing the concentration of either short chain prepolymer or that of the filler. Hence this study helps by providing a guideline for achieving optimum tear properties of the polymer network due to the reinforcement effect of filler as well as that of the bimodality for specific applications where high tear energy of the polymer network is needed.

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