Aspects of varying crosslinker and catalyst concentrations on tear strength of silicone polymer networks: Comparison of tear strengths using samples of different geometries

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ABSTRACT: Crosslinker and catalyst concentrations have been varied to prepare different hydroxyfunctional poly(dimethylsiloxane) (HOPDMS) polymer network compositions. The tear strengths of these silicone polymer networks have been measured using different geometries, as trouser, crescent, and Graves (angled) specimens. It has been observed that the results of tear strength of Graves and crescent-shaped specimens do not show a constant ratio with the concentration of crosslinker used for curing of HOPDMS networks. Instead, it has been observed and reported for the first time that the tear strengths of Graves and crescent-shaped samples show a crossover at about 1.2% crosslinker. The observation of this crossover pattern for different compositions of silicone networks show that it is difficult to compare the results of the tear test of the same polymer performed on samples of different geometries with one another. The crossover pattern of the tear energy results for the test specimens of two different geometries has been explained in the light of essential work facture theory based on the geometry of the testing sample, crosslinking, and testing that alters the distribution of force over the width of the specimen. It was shown that the change in composition of the HOPDMS networks changes the order of ranking of Graves and crescent tear tests. With varying catalyst concentration in the silicone network composition, the tear property differences between the Graves and crescent-shaped specimens are not significant. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43115.

INTRODUCTION

Rivlin and Thomas[1] extended the Griffith criterion of crack growth in brittle materials to polymers and determined the critical tearing energy for elastomers, analogous to the Griffith characteristic energy. The applied stress searches for a flaw, concentrates at that point, and then initiates the tear phenomenon. Every polymer is characterized by a specific energy per unit area of the torn surface created, and this is known as the critical tearing energy or strain energy release rate for that material.[2] A number of investigators[3–6] have shown that the critical energy for polymers is not dependent on the geometry and dimensions of the test sample and hence is considered to be a characteristic property of the material. Tearing energy includes surface energy, energy dissipated in plastic flow processes, and energy dissipated irreversibly in viscoelastic processes.[7]

Polymers and polymeric materials are ubiquitous and are now a part of our everyday life. The simulated mechanical properties of these materials predict their life endurance during a particular use. Among mechanical properties, the tear strength of these materials is an important property for this purpose because of its intrinsic nature. This property provides a basic understanding of the structure of the base polymeric material and the bonding of the additives (if any) with the base material and guides its potential uses in various aspects of day-to-day life. Some of the parameters that can affect the mechanical properties of polymers are the chemical structure, polymer chain lengths, crosslinks per unit volume, polymer chain entanglements, degree of orientation of polymer chains, thickness of the sample, the addition of filler (its size or nature), temperature of the testing sample, and the ratio of crystalline to amorphous regions. The tear resistance of a polymer film or sheet is a complicated function during the application of stress to rupture it. There are a number of tear test methods that differ from one another with respect to the geometries of the samples. For example, the British standards allow these tests with various geometries, such as trousers- and crescent-shaped and angled (Graves) specimens. The results of these tests are impressionistically thought to rank different polymer and polymeric materials

in the same order in spite of their different geometries and that the ratios of any two tear test results among them remain constant. Polymers and rubber-like materials have previously been extensively studied experimentally in various fracture modes.[7–9] For the case of tearing, the experimental and theoretical analyses have been performed.[4,10–14]

In order to test the above-mentioned notions, silicone networks having different compositions were prepared by using varying catalyst and crosslinker concentrations. These silicone networks were cut according to different standards in the form of different sample geometries and were tested for tear strength. The force-deflection behavior of a material was analyzed for determination of the tearing energy. The objective was to establish the existence of a relationship if any between the results of geometrically different samples from composition to composition of silicone networks. It is also of interest to see how the change in composition of silicone networks affects the order of ranking of different tear tests.

EXPERIMENTAL

Materials
The liquid hydroxyfunctional poly(dimethylsiloxane) (HOPDMS) prepolymer (silopren C50, $M_n = 88{,}000$) was supplied by Bayer Ltd. (Burghausen, Germany) The catalyst, dioctyltin maleate (DOTM) (LT195, $M = 459$), was supplied by Lankro Ltd. (Lancashire, UK), and the crosslinker vinyl tris (ethoxymethoxy) silane (VTEMS) (A172, $M = 280.4$) by Gelest, Inc. (Karlsruhe, Germany). The properties of the silopren C50 are given in the literature.[15]

A number of compositions were made by mixing the HOPDMS with catalyst and crosslinker. In one series, the concentration of catalyst was kept constant at 0.01% and that of the crosslinker was varied from 0.725 to 1.763%. In another series, a constant concentration of crosslinker, 0.5 g ($\sim$1%) was used for different compositions while that of the catalyst was varied from 0.026 to 1.141%. The range of concentrations of crosslinker was selected from the lowest amount of crosslinker that can cure the present silicone compositions to the higher level that could easily make a homogenous mixture. Similarly, the range of catalyst concentration was selected that could safely be weighed to the higher concentration that was expected to affect the tear properties to the optimum level. All of the compositions were cast onto a polyethylene plate and spread to a uniform film of about 1.4 mm thickness. A seven-day period was allowed to complete curing for all of the compositions in open air at room temperature. The seven-day duration allowed for completion of curing was chosen based on our experience during experiments for these compositions. After this period, the samples were not tacky and were felt to be fully crosslinked.

Using different sample geometries, the tear energies for silicone networks having various compositions, that is, one series with a varying amount of crosslinker and the other with a varying amount of catalyst, were measured from the respective force-deflection curves.

Method of Tear Property Measurements
The critical fracture energy, also called the tearing energy, is the energy spent per unit thickness per unit increase in crack length. During a tear strength measurement, the stress distribution at the tip of a tear crack is complex. It includes surface energy, energy dissipated in plastic flow processes, and energy dissipated irreversibly in viscoelastic processes. The total tearing energy is independent of the crack length and shape of the test specimen.[4,16]

The equations for determination of tear strength were derived from the trouser tear test based on a theoretical analysis of crack-growth behavior.[1,5,6,16,17]

The tear strength can be calculated from eq. (1)[4] as

$$T = \frac{2\lambda F}{h} - 2aW \qquad (1)$$

where λ is the extension ratio in the legs, F is the force required to propagate the tear at a given temperature, h is the torn thickness, $2a$ is the width of the test piece, and W is the elastic energy stored in the test sample. Assuming the extension in the test sample during the test is negligible, i.e., $\lambda = 1$, makes the elastic energy W equal to zero. This assumption simplifies eq. (1) to

$$T = \frac{2F}{h} \qquad (2)$$

Specimens for the tear tests were prepared from all of the compositions of silicone films. For the Graves and crescent test measurements, specimens were cut by respective cutters according to the British standards BS 903 Part A3:1982, and the trouser specimens were cut by a cutter according to British standard BS 903 Part A3: 1982. For the trouser tear test, specimens were prepared from the trouser cutter according to the British standard BS 6899: 1976. Five suitable specimens for each composition were selected for tear tests on the basis of visual inspection. Trouser, Graves, and crescent cutters were used for cutting the tear specimens according to the British Standard BS 6899:1976 and ASTM D624-54 Die C and B, respectively.

A Monsanto 500 rubber testing machine (Shakopee, USA) was used to measure the tear properties. The thickness of the torn portion of the specimen was measured with a micrometer. All of the tests were carried out at a strain rate of 50 mm/min using a sensitive 5 N cell, and the corresponding force-deflection curves were obtained from the chart recorder. Tear strengths were calculated from the respective curves. Out of the five test results for each composition, three modal values were taken, and their average was recorded as the representative of the tear test of the material.

RESULTS

Two series of HOPDMS networks have been prepared. One series was cured with a concentration of crosslinker ranging 0.725 to 1.763% while keeping the catalyst concentration constant (0.01%). The other series was cured using a constant (1%) amount of crosslinker and varying the concentration of catalyst (0.026–1.141%). The details of all these compositions along with the tear results of the corresponding silicone networks are presented in Tables 1 and 2.

Table 1. Variation of Tear Strengths with Crosslinker Concentration in HOPDMS Networks

Sample	% Crosslinker (A172)	Crescent (C) tear strength (KNm^{-1})	Graves (G) tear strength (KNm^{-1})	Trouser (T) tear strength (KNm^{-1})	C/G
1	0.725	1.342	0.814	0.187	1.649
2	0.853	1.602	1.189	0.145	1.347
3	0.923	1.768	1.601	0.134	1.069
4	0.999	1.961	1.631	0.129	1.202
5	1.101	2.130	2.037	0.112	1.045
6	1.184	2.232	2.152	0.122	1.037
7	1.31	2.251	2.631	0.11	0.855
8	1.378	2.261	3.072	0.123	0.736
9	1.584	2.333	3.13	0.116	0.745
10	1.763	2.232	3.013	0.107	0.741

In Tables 1 and 2, the tear results of HOPDMS networks have been categorized as (1) trouser and (2) Graves and crescent-shaped tearing. In the trouser tear test, there is a decrease in tear strength of about 40% with an increase in the concentration of crosslinker, followed by constancy in its values. In the case of HOPDMS cured with varying catalyst concentration, the trouser tear test again shows a decrease of about 40% in tear strength. These trends as depicted in Figures 1 and 2 are shown for trouser tear tests in both series of silicone networks, one with varying concentration of crosslinker and the other with varying concentration of catalyst.

As shown in Table 1 columns 3 and 4 and correspondingly depicted as Figure 3, both the Graves and crescent-shaped samples show first a linear increase in tear strength with an increase in concentration of crosslinker and then a leveling-off. This increase in tear strength for the crescent sample is recorded up to 1.375% use of crosslinker and for the Graves sample up to about 1.31%, after which they level off. The unique observation for these data is that the ratios of tear strengths of Graves and crescent-shaped samples are not constant for the compositions in series 1. Initially the tear strength of the crescent sample is greater than that of the Graves sample. However, as the concentration of crosslinker increases for curing of HOPDMS compositions, this difference in

tear strength decreases gradually from composition to composition. At a composition having about 1.25% crosslinker concentration, the tear strengths of both Graves and crescent-shaped samples become equal. A further increase of crosslinker concentration for curing of HOPDMS networks shows that the tear strength for the Graves sample becomes greater than for the crescent sample, and beyond this point the difference remains constant. These data show that for the Graves and crescent-shaped samples a crossover in the tear strength results is observed for HOPDMS cured with varying crosslinker concentration.

Correspondingly, Table 2 shows that the increase in tear strength of these two samples (Graves and crescent) with the increase in concentration of catalyst is not linear but in the form of a curve. The graphical representation of these data is depicted as Figure 4. This graph further displays that there is not much difference in the tear strengths of Graves and crescent samples with increase in concentration of catalyst used for curing of HOPDMS compositions. Tear strengths for both Graves and crescent-shaped samples show increases up to about 0.35% catalyst concentration, and then the values level off. The range of increase in tear property of HOPDMS networks for varying catalyst concentration is 1.3 to about 2.0 KN/m^2 and is smaller than that observed for the series with varying crosslinker concentration.

Table 2. Variation of Tear Strengths with Catalyst Concentration in HOPDMS Networks

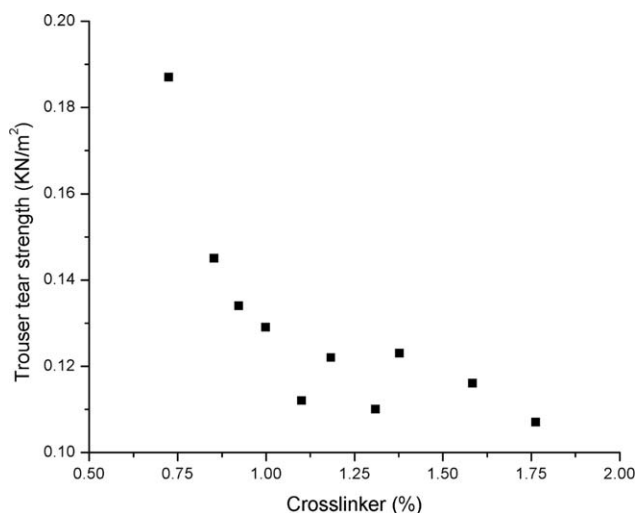| Sample	% Catalyst (LT195)	Crescent (C) tear strength (KN/m^2)	Graves (G) tear strength (KN/m^2)	Trouser (T) tear strength (KN/m^2)	C/G
1	0.026	1.439	1.343	0.142	1.071
2	0.056	1.507	1.476	0.135	1.021
3	0.066	1.559	1.629	0.126	0.957
4	0.119	1.65	1.741	0.115	0.948
5	0.196	1.823	1.812	0.1	1.006
6	0.302	1.847	1.895	0.093	0.975
7	0.359	1.96	1.982	0.089	0.989
8	0.539	2.001	2.06	0.089	0.971
9	0.685	2.052	1.984	0.083	1.034
10	1.141	2.014	1.952	0.075	1.032

Figure 1. Trouser tear strength variation of HOPDMS network with crosslinker concentration.

DISCUSSION

The two different categories of tear results, (1) trouser and (2) Graves and crescent-shaped specimens, present different patterns of properties for silicone networks having different compositions with respect to varying crosslinker and catalyst concentration. The trouser tear test shows a drastic decrease (about 40%), followed by leveling-off for HOPDMS networks with increases in crosslinker (Figure 1) and catalyst concentration (Figure 2). The decreasing trend of trouser tear strength with increase in concentration of crosslinker is in accordance with the established literature[18–22] based on the Lake–Thomas equation: $T \propto \bar{M}c^{1/2}$, where T is the tear strength and $\bar{M}c$ is the molecular weight between junctions of the polymer networks. As the increase of crosslinker and catalyst increase the curing, the $\bar{M}c$ decreases and so does the trouser tear strength.

The tear results of the Graves and crescent-shaped samples show increases with an increase in concentration of crosslinker (Figure 3)
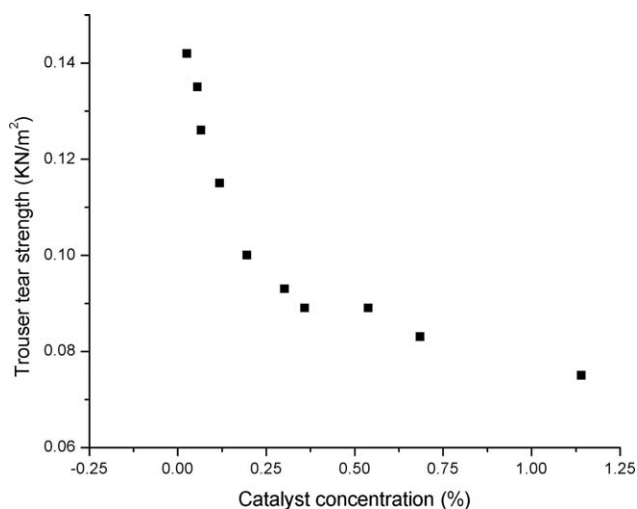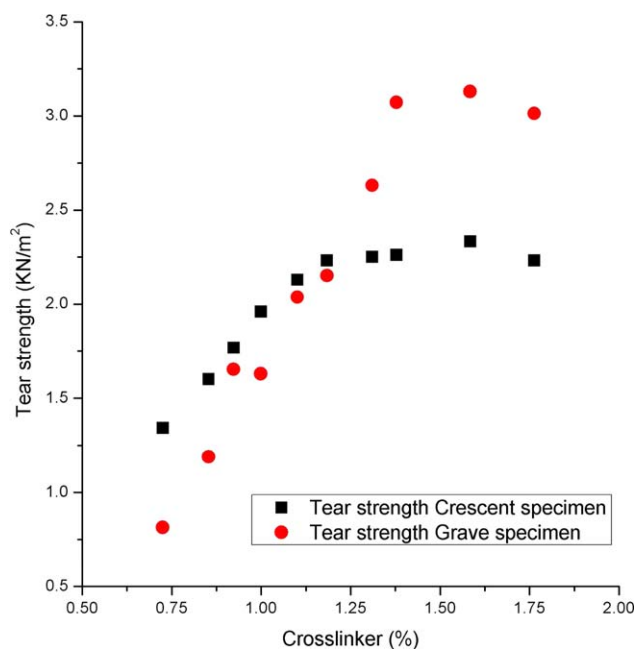

Figure 3. Tear strength variation of HOPDMS network with crosslinker concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and catalyst (Figure 4) up to a certain limit, and then the values show a leveling-off. In the case of Graves and crescent-shaped samples, their sample geometries make their tearing test akin to tensile-type testing. That is why the trends of the test results for variation of crosslinker and catalyst in HOPDMS networks show reverse trends as compared to that observed for trouser tear tests.

The differences in tearing strengths of the same polymer and polymeric materials according to sample geometry are implicit in their respective definitions. Trouser tear strength is the average force per unit thickness required to propagate a tear, whereas in the crescent and Graves samples, tear strength is defined as the
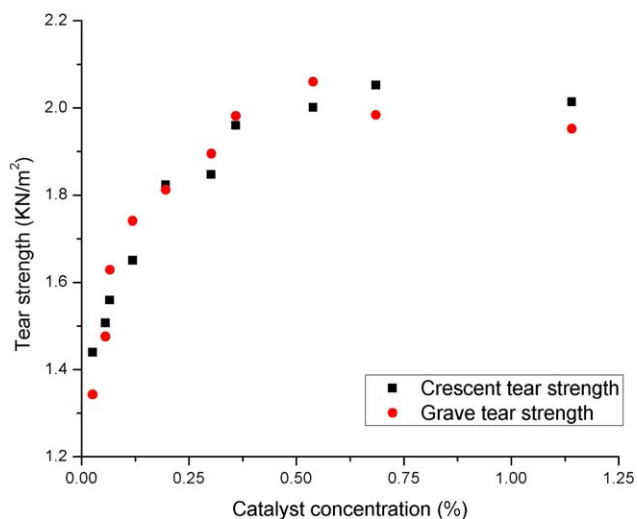

Figure 2. Trouser tear strength variation of HOPDMS with catalyst concentration.

Figure 4. Tear strength variation of HOPDMS network with catalyst concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

maximum force needed to rupture the specimen. In other words, the tear strength of Graves and crescent samples is akin to tensile testing by virtue of their geometry. Generally, tearing in rubber is known to initiate from an inherent flaw present in the rubber.[1] Upon stretching the polymer, the local stress in the vicinity of a flaw increases, which, when it reaches a critical or threshold level, initiates the tearing. This critical or threshold stress limit is specific for each material.

The change in the tear strength of Graves and crescent-shaped samples with varying crosslinker concentration in the composition of HOPDMS networks and their crossover with one another are interesting, novel, and newly reported. This pattern of crossover/transition of high tear strength for crescent samples to low tear strength, as compared to that of the Graves samples, associated with a change in composition of polymer networks has not been reported earlier for any type of elastomer. Initially (for compositions having low amounts of crosslinker), as presented in Figure 3, the tear strength of the crescent-shaped sample is greater than that of the Graves sample. Slowly and gradually, this difference in tear strengths is decreasing with an increase in concentration of crosslinker. At the threshold limit (for a network having 1.2% crosslinker), the tear strengths of the two types of samples become equal. A further increase in concentration of crosslinker makes the Graves sample stronger than the crescent sample in terms of tear strength.

The crossover of tear strength of these two types of samples can be explained as follows. If the tearing strength of the HOPDMS network is analyzed in terms of essential work facture theory,[7] then the measured total tear strength can be divided into two components: essential and nonessential tear energy. The essential tear energy is a characteristic of a particular composition of HOPDMS network and will not change with a change in geometry of the testing sample. The nonessential constituent energy is composed of energy dissipated in plastic flow processes and energy dissipated irreversibly in viscoelastic processes.[7] The geometry of the testing sample changes the ratio of these components. It is the variation of the ratio of these components of the nonessential tear energy with a change in geometry of the testing sample that differentiates the tear strengths of the same composition. Furthermore, the change in composition of the HOPDMS network (with change in crosslinker concentration) changes the tear strength. The interplay of change in composition of HOPDMS network, the fluctuation of the ratio of components of nonessential tear energy with change in geometry of the sample, is responsible for the crossover phenomenon.

The geometry of the Graves specimen is such that during the tearing process (due to stretching) most of the stress converges at the vertex of its angle, which makes it act as a nick. Silicone compositions cured with a low amount of crosslinker exhibit low tear strength; fracture occurs more easily in the Graves sample because the whole stress is directed to one point by virtue of its geometry. As the crosslinker concentration increases, the tear strength of the silicone networks gradually increases. The increased strength of the HOPDMS networks coupled with silicone being a good elastomer takes on the applied force and distributes it to the neighboring chains over the sample width

rather than concentrating it at one point, the vertex of the angle. This occurs at a threshold point corresponding to a specific composition of HOPDMS network from which onward the Graves specimen shows higher tear strength than the crescent-shaped sample. As the crosslinker increases, the rubber elasticity of silicone networks decreases, and the tear strength increases. As a result, the applied force does not concentrate at one point but is distributed uniformly over the whole width (12.5 mm) of the Graves sample, and hence the tear strength transforms somewhat to tensile-type behavior.

In the crescent-shaped sample (having simpler geometry than the Graves sample), the applied force is uniformly distributed over the width (10.5 mm) of the sample, so it gives a higher tear strength than the Graves specimen, even for the silicone networks cured with a low amount of crosslinker. After the crossover point, the Graves and crescent samples both tend to distribute the applied force over their respective widths. Because the width of the Graves sample (12.5 mm) is greater than the width of the crescent sample (10.5 mm), the tear strength of the former becomes greater.

The crosslinker concentration variation has shown a more pronounced effect in differentiating the results of the two geometries. The ratios of the tear strength of the crescent-shaped sample to that of the angled specimen show that it does not remain constant. However, for the second series, with variation of catalyst in silicone composition, the tear results of the two different sample geometries do not show any difference, and hence the crossover pattern like that for crosslinker variation is absent. The explanation for the deviation of this pattern from the first one could be that the composition of the HOPDMS network here is different. In the second series, the crosslinker amount is constant but exceeds by enough the required stoichiometric values for the compositions of the series. Similarly, the catalyst, which is usually required in small amounts, is also in a far more excessive range. It seems that the crossover pattern of the tear results of the Graves and crescent-shaped samples as observed for the first series of HOPDMS compositions is limited to the particular concentration range of crosslinker in the presence of a small amount of catalyst. It can also be seen that for the second series a greater dispersion of tear data is observed. The greater scattering of data in using an excessive concentration of catalyst for curing silicone is not new, and this has been reported earlier. The scattering of data in using an excessive amount of catalyst may have masked the differentiation, if any, between tear strengths of the Graves and crescent-shaped samples. That is why there is no obvious significant difference in results for the Graves and crescent-shaped geometries for varying concentration of catalyst.

CONCLUSIONS

Different compositions of HOPDMS in reference to using varying concentrations of crosslinker and catalyst have been cured and tested for tear strength. The following conclusions can be drawn from the present studies.

The different geometries of the tear specimens, trouser, Graves, and crescent, give different values of tearing strength for the

HOPDMS networks. The decrease in trouser tear strength with increase in concentration of crosslinker and catalyst in the HOPDMS network is in accordance with the Lake–Thomas equation. In the Graves and crescent-shaped specimens that are akin to tensile testing, the trend has been found to be in reverse order: tear strength increases with increase in crosslinker concentration.

A crossover in tear results for the Graves and crescent-shaped samples for silicone networks has been observed and reported. This type of phenomenon has for the first time been reported for an elastomer. The crossover pattern of the tear strength results of Graves and crescent-shaped samples for an HOPDMS series with crosslinker variation shows that these tests do not rank different compositions of silicone networks in the same order. The Graves and crescent specimens do not give a constant difference between tear strength for silicone networks over the entire range of crosslinker concentration used. The changes in composition of HOPDMS networks change the ranking order of the material from one geometrical test to another. It can be concluded that these different tear tests cannot be used for comparison of different materials.

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