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THERMAL TECHNIQUES TO STUDY COMPLEX ELASTOMER/FILLER SYSTEMS

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Abstract

The transfer of heat through an elastomeric matrix is important for both the processing of the material and its subsequent lifetime. Thermal conductivity can be used to evaluate the influence of different polymers and fillers on heat transfer. Additionally, the dispersion of the filler has an effect on heat transfer and thermal conductivity measurements can be used to provide semi-quantitative estimations of filler dispersion.

The degradation of sulfur-crosslinked elastomer systems has been studied for many years. The degradation of the crosslinks (changes in sulfur rank) and degradation of the polymer backbone by thermal and/or oxidative processes have been studied extensively using many techniques including thermal analysis (references). However, the degradation of the crosslinked-polymer ‘network’ is less well understood. The relationship of the crosslink network to this degradation process is a key to both the long term and higher temperature performance of the sulfur-crosslinked elastomer.

The changes in physical properties observed upon exposure of sulfur-crosslinked elastomers can be monitored using dynamic mechanical analysis. Subsequently, other thermal techniques can be used to monitor the chemistry that is occurring during these degradations. Thermal desorption/mass spectroscopy and dynamic scanning calorimetry are used to complete the picture of the degradation processes taking place. Examples of these techniques will be provided to illustrate the utility of the analytical approach, the chemistry involved in these degradation processes and the effect of changes in the polymer, cure package and other ingredients.

Keywords: degradation**,** differential scanning calorymetry, dispersion, dynamic mechanical analysis, fillers, thermal conductivity

Introduction

The lifetime of rubber products depends on several key factors. These include: the polymer matrix of the product, the ingredients added to the compound (fillers, extending oils, antidegradants, curatives, etc.), the network that holds the matrix together (crosslinks and polymer-filler interactions) and the heat history of the matrix. This nature of this complex composite determines both the thermal history that the compound will experience during use and the effect that the thermal history will have on the matrix.

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Obviously, the thermal history comes from both the heat build-up from hysteresis of the compound during stress/strain cycles and from the ability of the compound to transfer the heat for dissipation. The thermal conductivity of the matrix affects the heat transfer necessary during the mixing of polymer and ingredients. It is also important during the crosslinking of the network, affecting the nature of the crosslink network and its uniformity throughout the matrix. Finally, it is important in terms of the potential for degradation of the matrix during use. The hysteretic buildup of heat is a complex process and will not be discussed here. However, the transfer of heat from the compound relies on the thermal conductivity of the materials used in the compound. Because the materials used in these compounds have such widely different thermal conductivities, it is essential that the properties of the components and their distribution be understood in terms of thermal conductivity.

Once the thermal history of the matrix is understood in terms of heat build-up and heat transfer, then the degradation of the properties of the matrix can be dissected in terms of the changes in the matrix. Since the matrix consists of the polymers present, the crosslinks network, polymer-filler interactions and the other ingredients of the compound, several different mechanisms are involved in the changes in physical properties observed. A great deal of literature exists for the thermal and oxidative degradation of polymers [1–4]. Additionally, the changes of the crosslink network, referred to as thermal 'reversion', have been studied extensively in terms of the change in crosslink density, crosslink rank and main chain modification [5–11]. More recently, there have been some studies looking at the oxidation of the crosslinking network including the effects of antioxidants [12–15] specifically for sulfur-crosslinked networks [12–14]. However, the interaction of the polymer and the crosslink network (specifically sulfur-crosslinked networks) resulting in degradation at higher temperatures has received little attention in the literature.

The discussion in this paper will center on two aspects of this complex problem. The first part will focus on the thermal conductivity of elastomer matrices with fillers examining both filler content and distribution. The second part will focus on the degradation of the polymer-crosslink network that occurs at high temperatures. This investigation will include both determination of the mechanism of the degradation and evaluation of a means to obviate the serious changes in physical properties that result from this degradation.

Because elastomers do not conduct heat very efficiently, there are instances in tires where this heat build-up results in the tire component reaching temperatures where significant degradation occurs. A more complete understanding of this process and what can be done to mitigate it is important for applications where heat build-up occurs. Dynamic mechanical analysis can be used to detect where these types of degradations are taking place and to provide details on the thermal thresholds involved. Thermal desorption with GC/MS analysis of by-products provides a tool to understand the chemistry involved.

Experimental

Materials

The polymers used in this study were Natsyn 2200 (IR), Budene 1207 (BR), Plioflex 1502 (SBR) – all supplied by Goodyear – and a standard grade of Natural Rubber (NR). The carbon blacks were all ASTM grades of carbon black. The curatives were all standard curative chemicals typically used in the industry. Perkalink 900©, a bis-citraconamide from Flexsys, was also used. All materials were used as received.

Compounding

All compounded stocks were mixed in standard laboratory batch mixers. The amount of any component in the compound is expressed as 'phr', parts per hundred parts of rubber. Mixing conditions were: non-productive mixes – 3 min at 55 rpm at 100°C; productive – 3 min at 35 rpm at 60°C. All samples were milled after mixing and cured to t90 (90% of maximum cure) at 150°C in a compression mold.

Thermal conductivity

All thermal conductivity measurements were conducted using a Holometrix TCA unit. Samples (50 mm diameter, 1 cm thick) were cut from cured sheets and placed in the unit. DOW 340 cream (silicon heat sink compound) was applied to the sample in contact with the instrument to assure uniform thermal contact. Samples were scanned from 60 to 150°C with laser correction of thickness recorded at each temperature jump. Calculations were done using a custom spreadsheet.

Thermal analysis

Dynamic mechanical analysis (DMA) was conducted using a Rheometrics DMTA IV unit in compression mode. The samples were 0.7×0.7 mm cylinders. Temperature sweeps were conducted at 11 Hz at 4% strain with a scan rate of 3°C min^{-1} from 30 to 250°C. Differential scanning calorimetry (DSC) was conducted on a TA Instruments 912 Dual Sample DSC in hermetically sealed aluminum pans up to 275°C under nitrogen.

Thermal desorption

Samples were thermally extracted (desorbed) in helium with the desorbed volatiles cryo-trapped and subsequently chromatographed using mass spectrometry detection. Samples of 9.3 mg were employed with 10.0 min desorption times for all temperatures (160, 190, 220°C) providing semi-quantitative data on the materials generated. The 'relative amount' is the numerical response of the peak in the gas chromatography data for the collected sample. Since these values are not strictly quantitative, the term 'relative amount' is used to indicate the approximate amount of the material isolated.

Results and discussion

Thermal conductivity studies

The thermal conductivity studies conducted here consist simply of placing a sample between two platens under pressure, heating one platen and measuring the heat flow through the sample during this process. Using the Eqs (1) and (2), it is possible to calculate the thermal conductivity, k, from the heat flow and thickness of the sample. The silicon heat sink compound is present to minimize the R_0 value the experiment. Since the samples are under pressure, the value of d can change and is monitored by a laser measurement device to correct this during the test.

$$R_s = N\frac{(T_u - T_l)}{Q} - R_0 \qquad (1)$$

where R_s, R_0 are sample and adjoining surfaces thermal resistance (using a basis of m^2), Q is the heat flow transducer output, T_u, T_l are upper and lower platen temperature and N is a proportionality constant.

$$R_s = \frac{d}{k} \qquad (2)$$

where d is the sample thickness and k is the sample thermal conductivity.

After examining a series of cured polyisoprene (IR) samples (Fig. 1) with varying levels of carbon black at different temperatures, it is obvious that the temperature of the sample has little effect on the thermal conductivity while the carbon black level does have a significant effect. Since carbon black has a much higher thermal conductivity than the polymer matrix, these results are expected. Similar results were obtained with other polymers such as polybutadiene (BR) and styrenebutadiene rubber (SBR) with small variations based on the thermal conductivity of the polymer. Similar results were also noted for silica-containing compounds with slightly lower values, based on the lower thermal conductivity of silica.

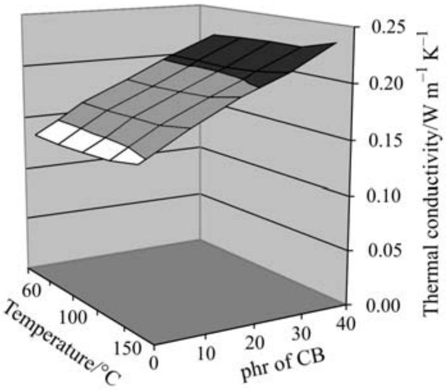

Fig. 1 Thermal conductivity of cure polyisoprene with varying carbon black content

Another series of samples were prepared where different carbon blacks were incorporated into a compound and the thermal conductivity was evaluated. These carbon blacks had different surface area and structure values (as determined by ASTM methods). The results of this study (Table 1) did not show any obvious correlation between either surface area or structure and the thermal conductivity values.

Table 1 Thermal conductivity of polyisoprene with 13% *v*/*v* of various carbon blacks[a]

Carbon black ASTM designation	Surface area/ $m^2\ g^{-1}$	Structure/ cc 100 g^{-1}, DBP	Thermal conductivity/ $W\ m^{-1}\ K^{-1}$	Dispersion (rating 1–10)
N110	142	127	0.192	5.3
N220	121	114	0.195	8.0
N299	108	124	0.193	8.3
N326	82	72	0.192	4.1
N660	36	91	0.198	9.2

[a] thermal conductivity value for polyisoprene is 0.14 $W\ m^{-1}\ K^{-1}$, the value for the carbon blacks is estimated to be ~100 $W\ m^{-1}\ K^{-1}$

Because most compounds used in the rubber industry are composed of two or more polymers, the effect of distribution of the carbon black in the blend on thermal conductivity was also of interest. A series of samples were prepared where two polymers (IR and BR) were blended in various ratios with a constant carbon black content of 40 phr Fig. 2. The thermal conductivity values for the blends did not follow the predicted average value for the pure polymer compositions. The reason for this discrepancy is attributed to the distribution of the carbon black in the blend. If the distribution favors one phase over the other, the pathway for heat transfer could be disturbed and lead to lower values than predicted.

To examine this possibility, another series of samples was mixed where the carbon black was introduced in varying ratios in the two polymers. Three compounds were mixed with 50:50 ratios of polybutadiene and polyisoprene. In two compounds

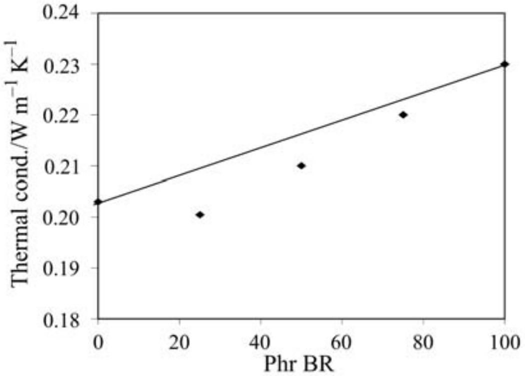

Fig. 2 Thermal conductivity of blends of IR and BR with 40 phr carbon black

the carbon black was introduced into the separate polymers first (phase mixing), providing twice as much carbon black to one of the two polymers. These were then mixed and the final compound examined. In a third compound, all the carbon black was introduced into both polymers at the same time. These results were compared with the same carbon black level in the pure polymers. As seen in Fig. 3, the compound where the carbon black was randomly mixed into the two polymers had a thermal conductivity value below the average of the two pure polymers. When the carbon black was phased mixed into the two polymers, there are further differences from the random mixing scheme. When more carbon black was introduced into the polybutadiene phase, the thermal conductivity was higher while the opposite was true when more carbon black was introduced in the polyisoprene phase. These results indicate that the polyisoprene retains more carbon black and that the method of introducing the carbon black into the compound can lead to a greater or lesser heterogeneity in the distribution of the carbon black in the compound.

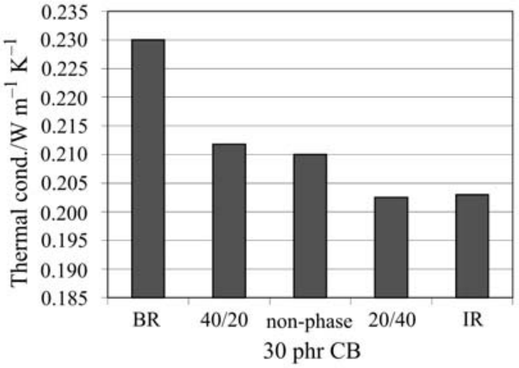

Fig. 3 Thermal conductivity of 50:50 blends of IR/BR with various carbon black incorporation schemes

The fact that the thermal conductivity can be affected by the distribution of carbon black in the compound two polymers would also indicate that dispersion of carbon black (a measure of mixing efficiency) might also affect the thermal conductivity of a compound. To examine this, compounds with only polyisoprene were mixed with two levels of carbon black. Two mixing protocols were used to produce both poor mixing (short mix time, slow rotor speed) and good mixing (longer mixing time, faster rotor speed) in an attempt to affect the dispersion of the carbon black in the compound. The dispersion was measured along with the thermal conductivity. As seen in Fig. 4, at low levels of carbon black (10 phr), the dispersion of carbon black is poor for both compounds and the thermal conductivity is not very different for the two compounds. This would be expected because the low level of carbon black does not result in significant shear and poor mixing results. At the higher level of carbon black (40 phr), the mixing is more efficient with the good mixing protocol and the dispersion is much better. As a result, the thermal conductivity of the well dispersed compound is significantly higher than for the poor dispersion sample. These results indicate that it might be possible to

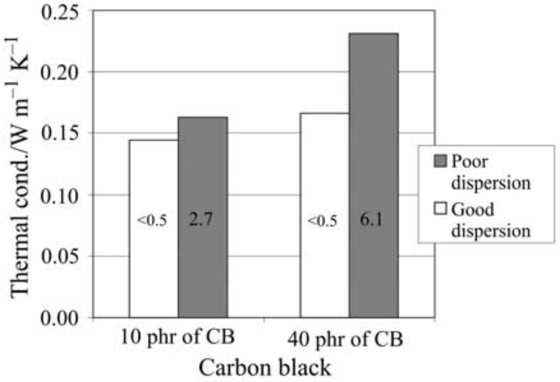

Fig. 4 Dispersion and thermal conductivity for polyisoprene compounds with different mixing protocols

use thermal conductivity to measure variations in dispersion of fillers. Some work has been done in this area and is worth pursuing [16–24].

Although the thermal conductivity of rubber compounds is dominated by the reasonably poor thermal conducting rubber, it is a useful tool that can be used to predict heat transfer during mixing, curing and use. Additionally, dispersion can be at least qualitatively measured using this tool.

Degradation of physical properties

The fact that rubber compounds do not transfer heat very effectively leads to the problem that heat builds up during use and can be problematic for extended use. Many applications result in considerable heat build-up and the temperatures reached can lead to considerable degradation. When a sulfur-cured elastomer compound is heated, the properties go through a series of stages. As shown in Fig. 5, from room temperature to about 100°C (low temperature regime), there is a slight drop in E' and tanδ, primarily from thermal softening of the polymer matrix. From 100 to 180°C (mid-temperature regime), there is an increase in E' that can be associated with rearrangement of the crosslink network involving a decrease in sulfur rank of the crosslinks and an increase in the crosslink density. These two phenomenons are both reasonably well understood. From 180 to 220°C (high temperature regime), there was a significant drop in E' and an increase in tanδ. These two effects were believed to be the result of degradation of the crosslinked elastomer. As also seen in Fig. 6, when the nature of the curative system is changed from a standard cure system (relatively high in sulfur) to an efficient cure (EV) system (relatively low in sulfur), the typical increase in stiffness observed in the mid-temperature regime is not seen and the drop in the high temperature regime is mitigated. This result hints at the role of the sulfur crosslinks in the degradation mechanism.

Finally, in Fig. 7, the effect of varying the sulfur content is seen. When low levels of sulfur are used, the initial E' values are low but the same drop in E' is noted at

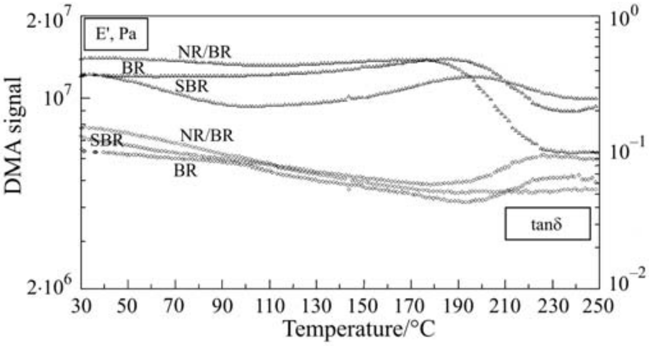

Fig. 5 DMA curves of NR/BR, BR and SBR compounds

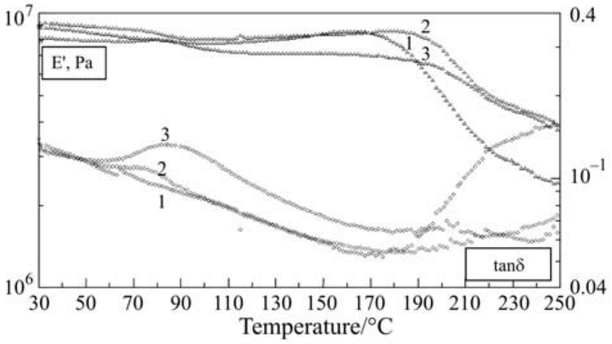

Fig. 6 DMA curves of NR/BR compounds with different cure systems (1 – standard cure, 2 – semi-EV cure, 3 – EV cure)

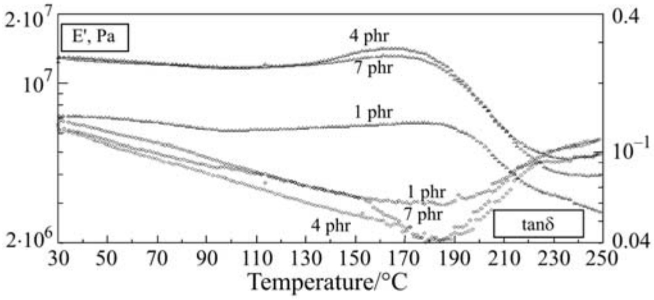

Fig. 7 DMA curves of NR/BR compounds with varying sulfur content

the higher temperatures. When the sulfur level is increased, the *E*' in general is increased but the drop in *E*' at the higher temperatures is even more significant and only increases with higher levels. Again, these results point to a significant role of sulfur in these degradations.

To examine the nature of this degradation, samples of both gum rubber and sulfur-crosslinked rubber were both thermally desorbed at 220°C to examine the degradation by-products. As seen in Fig. 8, gum rubber shows almost no volatile material

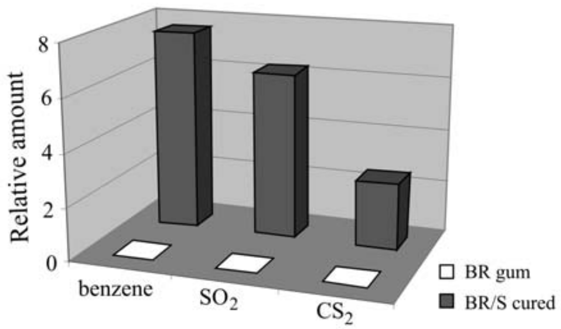

Fig. 8 Thermal desorption of BR rubber with and without sulfur curing at 220°C

during high temperature treatment. However, the presence of sulfur crosslinking leads to significant generation of sulfur-based by-products and the generation of benzene. When the same experiment is conducted using IR or NR, the same general result is obtained except that *m*-xylene is generated instead of benzene. The presence of SO_2 in these samples is derived from some previous oxidation of the sample prior to this thermal desorption experiment. Oxidation of crosslinks is known and may partially explain the detection of this molecule.

To determine if this sulfur-based degradation was dependent on temperature, a series of samples were thermally desorbed at different temperatures. As seen in Fig. 9, in the mid-temperature range (160°C), there was no benzene generated while at the elevated temperatures of 190 and 220°C, there was noticeable benzene generated which increased with increasing temperature. This indicated that the generation of the benzene (or *m*-xylene) in the sulfur-crosslinked rubbers was linked to the degradation seen in the DMTA. Additionally, an analysis of the degradation by-products as a function of the sulfur level of the compound also shows that the sulfur is directly related to the level of by-product generated (Fig. 10).

The degradation mechanism that explains these results involves dehydrogenation of the polymer backbone during the breakdown of the sulfur crosslinks [25–28]. As shown in Fig. 11, the polyenes that are generated during this dehydrogenation eventually are involved in a cyclization process that eliminates the aromatic molecules detected by thermal desorption. With this mechanism explaining the degrada-

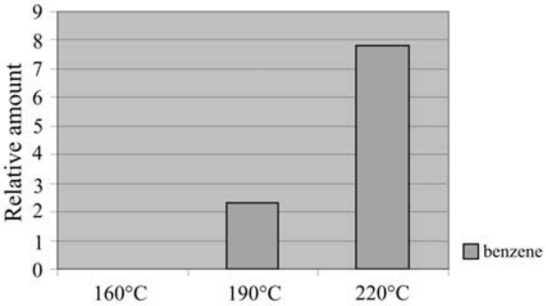

Fig. 9 Thermal desorption of BR at different temperatures

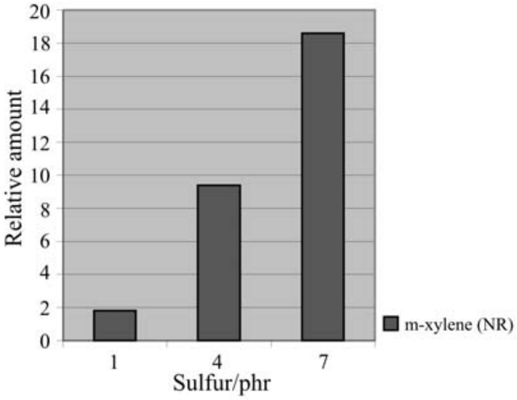

Fig. 10 TG/GC/MS for NR with varying sulfur levels

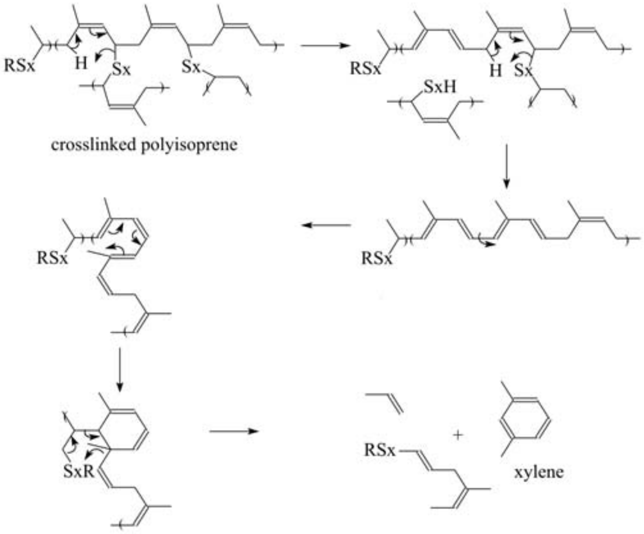

Fig. 11 Degradation mechanism for sulfur-crosslinked diene polymers

tion at these elevated temperatures, it provides an opportunity to chemically interfere with the degradation and reduce the overall effects of elevated temperature. Perkalink 900$^{©}$, a commercially available bis-citraconamide material, is reported to be capable of reacting with di- and trienes and, because it is difunctional, could replace the degraded crosslink (Fig. 12).

To test this idea, varying levels of this additive were used in a sulfur-crosslinked rubber compound and the physical response was examined by DMTA. As seen in Fig. 13, as the level of the additive was increased the size of the drop in stiffness (*G*') noted above 190°C decreased. There was an accompanying decrease in the rise in tanδ also. When thermal desorption experiments were conducted (Fig. 14) on these same samples, the amount of the aromatic molecule isolated also decreased. These results in-

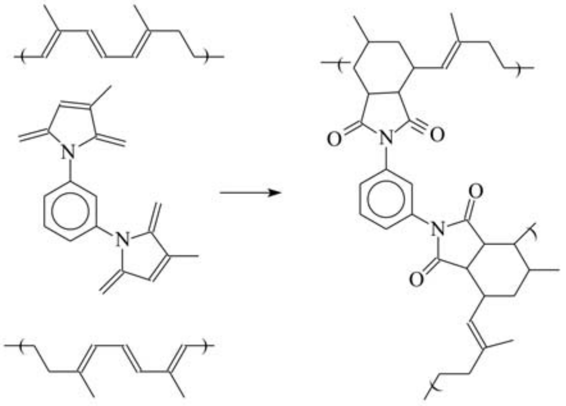

Fig. 12 Proposed mechanism of action for Perkalink 900© with dienes and trienes

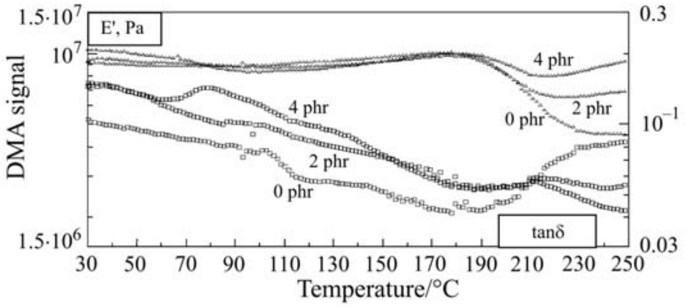

Fig. 13 Effect of varying the Perkalink 900© level in sulfur-crosslinked NR/BR compounds (3 phr sulfur)

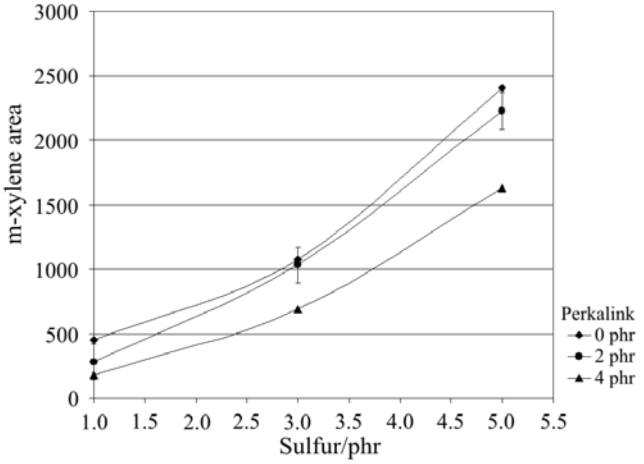

Fig. 14 Effect of Perkalink 900© level on xylene production during degradation of NR compounds

dicate that the bis-citraconamide additive is intercepting the dienes and trienes and reforming crosslinks between polymer chains. The replacement of the sulfur crosslinks by this mechanism leads to a smaller decrease in overall crosslink density and retention of the stiffness of the compound as well as mitigation of the increase in hysteresis.

The reaction of the bis-citraconamide with the polymer can be detected by DSC as a post-cure exotherm, closely associated with the breakdown of the crosslink network (Fig. 15). These two compounds have already been cured to maximum cure and the exotherm observed to start at about 190°C is associated with the degradation and new bond formation. The sample with no Perkalink 900© shows a modest exotherm, resulting from the degradation of the matrix. When there is Perkalink 900© present, the size of the exotherm increases. The size of the exotherm reflects both the level of sulfur in the compound (level of degradation) and the level of the bis-citraconamide present (level of new bond formation).

When a design of different levels of sulfur and Perkalink 900© was mixed and the resulting cured compounds were examined by DSC, the size of the exotherm noted in the 190–250°C temperature range increased with increasing sulfur content and increasing Perkalink 900© content (Fig. 16). This trend is expected based on the chemistry involved.

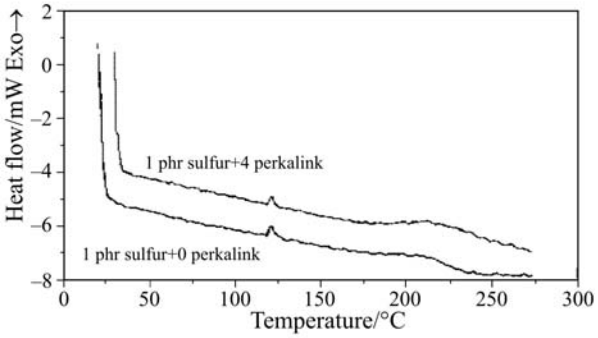

Fig. 15 DSC curves for a NR compound (1 phr sulfur) with different levels of Perkalink 900©

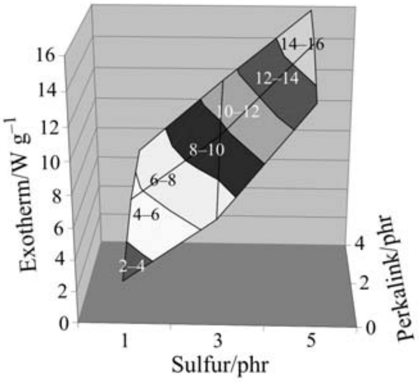

Fig. 16 DSC exotherm as a function of sulfur and Perkalink© used (temperature range of 190–250°C)

Conclusions

The transfer of heat through an elastomeric matrix is important for both the processing of the material and its subsequent lifetime. Thermal conductivity can be used to evaluate the influence of different polymers and fillers on heat transfer. Additionally, the dispersion of the filler has an effect on heat transfer and thermal conductivity measurements can be used to provide semi-quantitative estimations of filler dispersion.

Heat build-up during use of elastomeric compounds is another important factor in material lifetime. The degradation of sulfur-crosslinked rubbers at elevated temperatures involves a dehydrogenation caused by the crosslinks themselves. This degradation leads to the generation of aromatic molecules as by-products. This process can be mitigated by the use of reactive materials that intercept the intermediate dienes and trienes generated, such as Perkalink 900©. The degradation of the sulfur-crosslinked rubber can be characterized by DMTA, DSC and thermal desorption techniques, providing useful information on the mechanisms.

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