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Reinforcement of Elastomer by Reactive Ionic Surfactant

WHC Honors Research Project

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Abstract

Elastomers without cross-linking agents or fillers do not have the necessary properties for practical applications in the rubber industry. Elastomers must be reinforced with fillers and/or cross-linking agents to achieve the needs of physical and mechanical properties for commercial products. Sodium octyl 6-mercaptohexyl phosphate (SOMP) and sodium ethyl (6-mercaptohexyl) phosphate (SEMP) were used to investigate the influence of a reactive ionic surfactant and its influence on the physical properties of peroxide crosslinked styrene butadiene rubber (SBR). SEMP and SOMP were both found to be able to be grafted successfully on to the SBR chains within the rubber using extraction testing and IR spectra analysis. The two surfactants also improved mechanical strength properties of SBR when mixed at various concentrations using tensile testing. More research needs to be pursued in this area to find the optimum concentration of each surfactant while mixed in rubber. Blends of these two surfactants could also be considered. Other ionic compounds can be investigated in hopes of better physical crosslinking and ease of use small scale and eventually large scale.

Introduction

Elastomers without cross-linking agents or fillers do not have the necessary properties for practical applications in the rubber industry. Elastomers must be reinforced with fillers and/or cross-linking agents to achieve the needs of physical and mechanical properties for commercial products. Sodium octyl 6-mercaptohexyl phosphate (SOMP) and sodium ethyl (6-mercaptohexyl) phosphate (SEMP) were used to investigate the influence of a reactive ionic surfactant and its influence on the physical properties of peroxide crosslinked styrene butadiene rubber (SBR). SOMP and SEMP were chosen due to previous knowledge of synthesis and reactivity with different type of rubbers, including SBR. Dicumyl peroxide (DCP) is a cross-linking agent used in the formulation of each surfactant/SBR sample. Varying DCP can vary the crosslink density and possibly extent of reaction of surfactant to the rubber. The goal of the project was to determine whether SEMP or SOMP could physically crosslink with SBR and whether it created a stronger material than unmodified SBR.

Previous research by Qian [1] has been essential to the advancement of this stage of the research. We found that SOMP was not capable of reacting with cis 1,4-polyisoprene. However, due to the promising research of the surfactant itself, it was decided to continue using SOMP and other similar surfactants with other types of rubber including SBR.

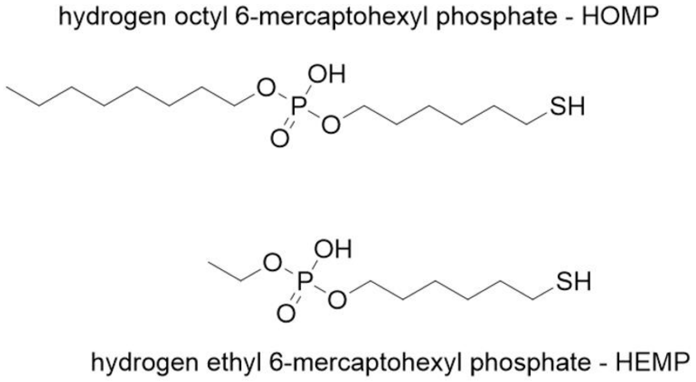
Experimental Methods

Synthesis of SOMP/SEMP

In a 200 mL Schlenk reaction flask, 0.05 mol phosphoryl chloride ($POCl_3$) and 100 mL anhydrous diethyl ether were added under nitrogen. The flask was placed in an ice bath. In another flask under nitrogen as well, 0.05 mol anhydrous alcohol, ethanol or octanol, and 0.05 mol anhydrous triethylamine was mixed. The second mixture was then added dropwise to the reaction flask. The reaction continued for 30 minutes. Precipitation of triethylammonium chloride was noted. A third flask of 0.05 mol 6-mercapto-1-hexanol and 0.05 mol anhydrous triethylamine was mixed under nitrogen. The contents of the third flask were then added dropwise to the reaction flask. The reaction was allowed to proceed overnight (approximately 18 hours), and the ice bath was allowed to come to room temperature (20° C).

The crude product was separated from the triethylammonium chloride precipitate by filtration. 0.25 mol of DI water was added to the mixture and mixed for 2 days at room temperature. After 2 days, another 30 mL of water was added to the solution and the aqueous phase was extracted with 20 mL of diethyl ether 3 times. The diethyl ether was removed via vacuum. The experiment yielded 10.90 g hydrogen ethyl 6-mercaptohexyl phosphate (HEMP) or 14.44 g hydrogen octyl 6-mercaptohexyl phosphate (HOMP). These are intermediate products of SEMP and SOMP, respectively. The molecular structures of these products are in **Fig. 1**. HEMP produced a 90.0% yield and HOMP produced an 88.5% yield.

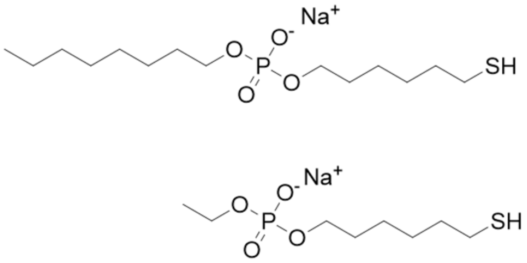
50 mL ethanol was added to HEMP (or HOMP) to dissolve the intermediate products. Then, a 0.1 M solution of sodium hydroxide in ethanol was added dropwise until the solution was neutralized. The solvent was then removed via vacuum. A crude final product was collected at this point of 11.96 g SEMP and 15.47 g SOMP. The product was finalized using 45 mL chloroform to either SEMP or SOMP and then reprecipitated in 450 mL hexane. The temperature of the solution was reduced to -45°C. The liquid was then decanted from the product. The product was then dried via vacuum. The molecular structures of SEMP and SOMP are in **Fig. 2**. Final collection of products revealed an 82.0% yield or 10.84 g of SEMP and a 72.5% yield or 12.63 g SOMP.


hydrogen octyl 6-mercaptohexyl phosphate - HOMP

hydrogen ethyl 6-mercaptohexyl phosphate - HEMP

Figure 1. The figure above shows the molecular structure of the intermediate products, hydrogen ethyl 6-mercaptohexyl phosphate (HEMP) and hydrogen octyl 6-mercaptohexyl phosphate (HOMP) created during the synthesis of sodium octyl 6-mercaptohexyl phosphate (SOMP) and sodium ethyl (6-mercaptohexyl) phosphate (SEMP).

sodium octyl 6-mercaptohexyl phosphate - SOMP



sodium ethyl 6-mercaptohexyl phosphate - SEMP

Figure 2. The above figure shows the molecular structures of the final products sodium octyl 6-mercaptohexyl phosphate (SOMP) and sodium ethyl (6-mercaptohexyl) phosphate (SEMP).

Compounding and vulcanization

The formulations of rubber compounds are shown in **Table 1**. BUNA VSL 5025-2 HM (96.25 parts per hundred rubber (phr)) and Budene 1207 (30 phr) were both mixed in a Masterbatch for all compounds. BUNA VSL 5025-2 HM has 26.25 phr oil in it while Budene 1207 has 0 phr oil in it. Each rubber compound was first solution mixed in 1-L beaker with approximately 600 mL of chloroform, SBR, and X phr of the surfactant. The solution was allowed to mix for 1 day until incorporated. The solvent was then allowed to evaporate over approximately 2 days at room temperature and then pumped under vacuum for 3-5 days. Once dry, the rubber compound was milled on a two-roll mill at 50°C with 0.3 phr DCP. The finished compound was cured at 160°C for 30 minutes to form sheets on a curing press. The curing time was measured using moving-die rheometer.

Table 1. Formulations of rubber compounds

Compound	**Masterbatch SBR (phr)**	**SOMP (phr)**	**SEMP (phr)**	**DCP (phr)**
0 phr Surfactant (Unmodified)	100	0	0	0.3
5 phr SOMP	100	5	0	0.3
15 phr SOMP	100	15	0	0.3
5 phr SEMP	100	0	5	0.3
10 phr SEMP	100	0	10	0.3
15 phr SEMP	100	0	15	0.3

Moving-Die Rheometer

Moving-Die Rheometer (MDR) was used to measure the curing curve of different rubber at 160 ^{o}C for 45 minutes. Under a constant amplitude (7% strain) of oscillation at a given temperature, vulcanization is measured by the increase of torque.

Tensile Test

Tensile specimens were cut with an ASTM D412 Type C dumbbell die. Dumbbell samples were held with a 70 mm gap distance and attached extensometer with the initial gap of 20 mm was applied to measure the strain. Three tensile specimens were assessed in each case. The crosshead speed was 50 mm/min.

Extraction Test

About 0.5 grams of cured sample was weighed and immersed in chloroform for 5 days at room temperature. The chloroform was exchanged twice within this time period. The solvent taken from the samples was dried and the left-over material was characterized via NMR.

Stress Relaxation

Stress relaxation was used to determine the crosslink density of each sample. Approximately 0.5 grams of cured sample was weighed and immersed in THF to remove oil. The THF was exchanged twice. The experiment was done at 60 ^{o}C at 5% strain.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was used to characterize the viscoelasticity and the glass transition temperature of the rubber. A temperature sweep was completed with a range of -50 °C to 175 °C at a 5% strain, 1 Hz, and 3 °C/min.

Results and Discussion

Overall, six rubber samples were formulated using the recipes found in **Table 1**. Three of them were SEMP samples ranging from concentrations of 5 phr to 15 phr. Two SOMP samples were made at 5 phr and 15 phr concentrations.

Curing Kinetics of SEMP

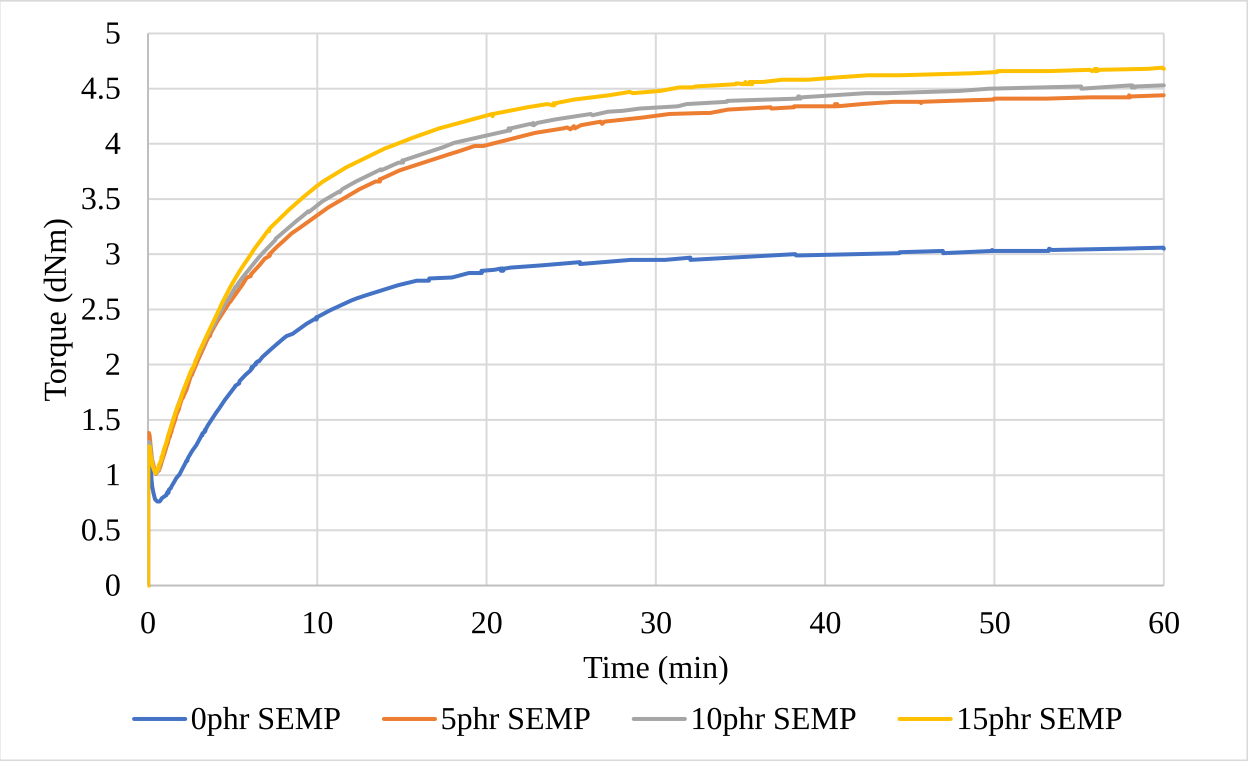


Figure 3. The figure above shows the curing kinetics of SEMP.

Using MDR, the curing kinetics were found for all SEMP samples. From **Fig. 3** above, one can see that the t_{90} for each sample was about 30 minutes. This result confirmed that the cure time for each sample should be 30 minutes. As the concentration of SEMP increases, the torque also increases as seen in **Fig. 3**. There is not a very large increase in torque when changing concentration between 5 phr to 15 phr however. This difference seen is statistically insignificant due to the testing methods reproducibility of ASTM D5289. The difference seen between 0 phr and 5 phr is significant, however. The surfactant increases the torque which signifies a stiffer rubber.

Curing Kinetics of SOMP

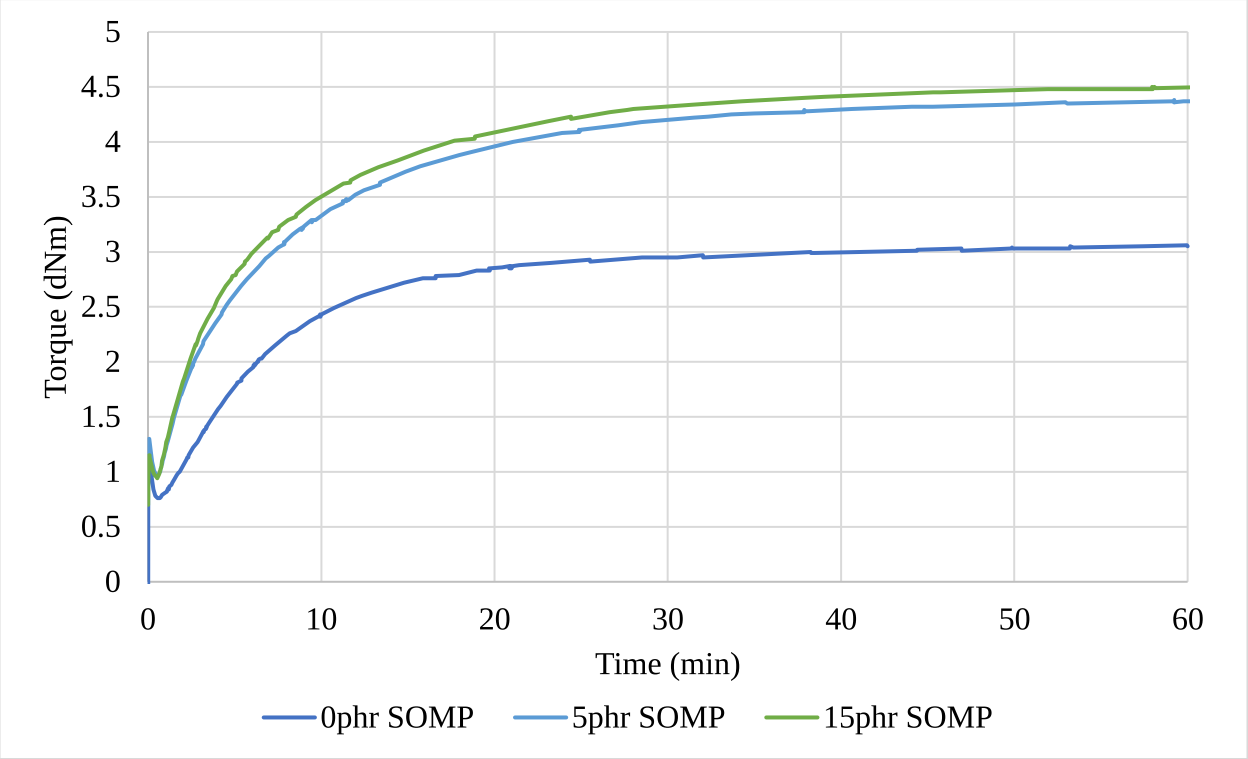


Figure 4. The figure above shows the curing kinetics of SOMP.

Using MDR, the curing kinetics were found for all SOMP samples. From **Fig. 4** above, one can see that the t_{90} for each sample was 30 minutes. This result confirmed that the cure time for each sample should be 30 minutes. As the concentration of SOMP increases, the torque also increases as seen in **Fig. 4**. There is not a very large increase in torque when changing concentration between 5 phr to 15 phr however. This difference seen is statistically insignificant due to the testing methods reproducibility of ASTM D5289. The difference seen between 0 phr and 5 phr is significant, however. The surfactant increases the torque which signifies a stiffer rubber.

Tensile Curves of SEMP/SOMP

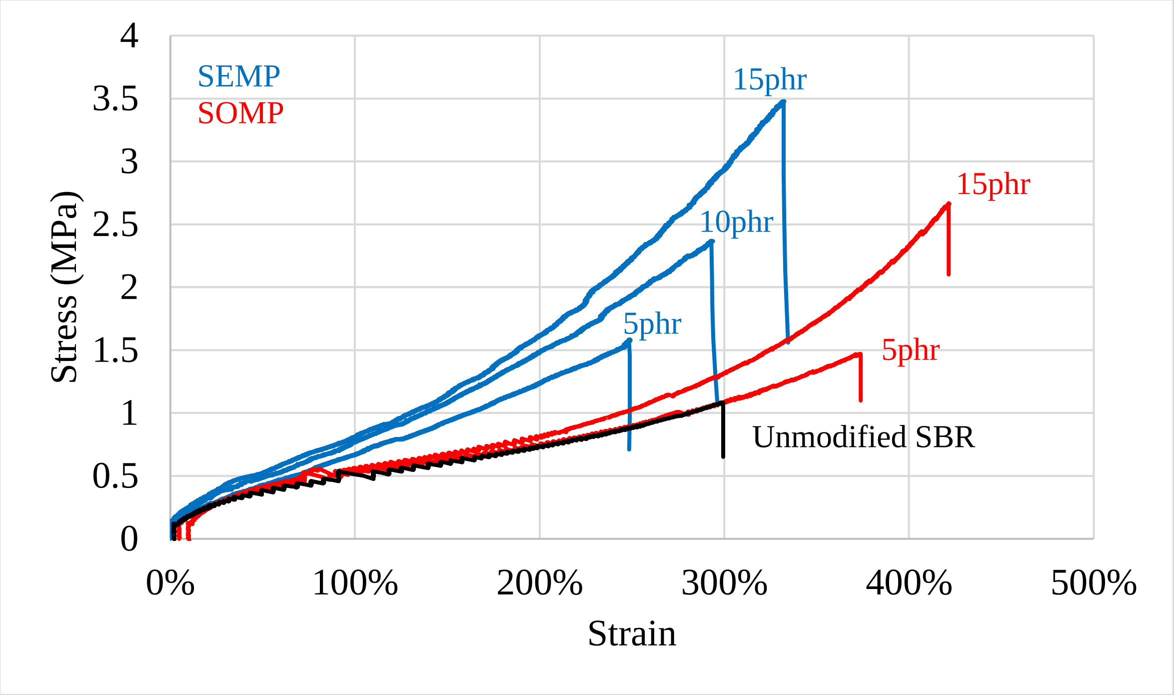


Figure 5. The figure above shows the representative curves for all rubber compounds tested. The blue curves show SEMP in SBR as various concentrations. The red curves show SOMP in SBR at various concentrations.

From **Fig. 5**, the smaller surfactant, SEMP, modified with SBR has better reinforcement properties than the larger surfactant modified with SBR. All modified SBR compounds had better reinforcement properties than unmodified SBR. SEMP and SOMP are reinforcing the compound.

DMA of SEMP/SOMP

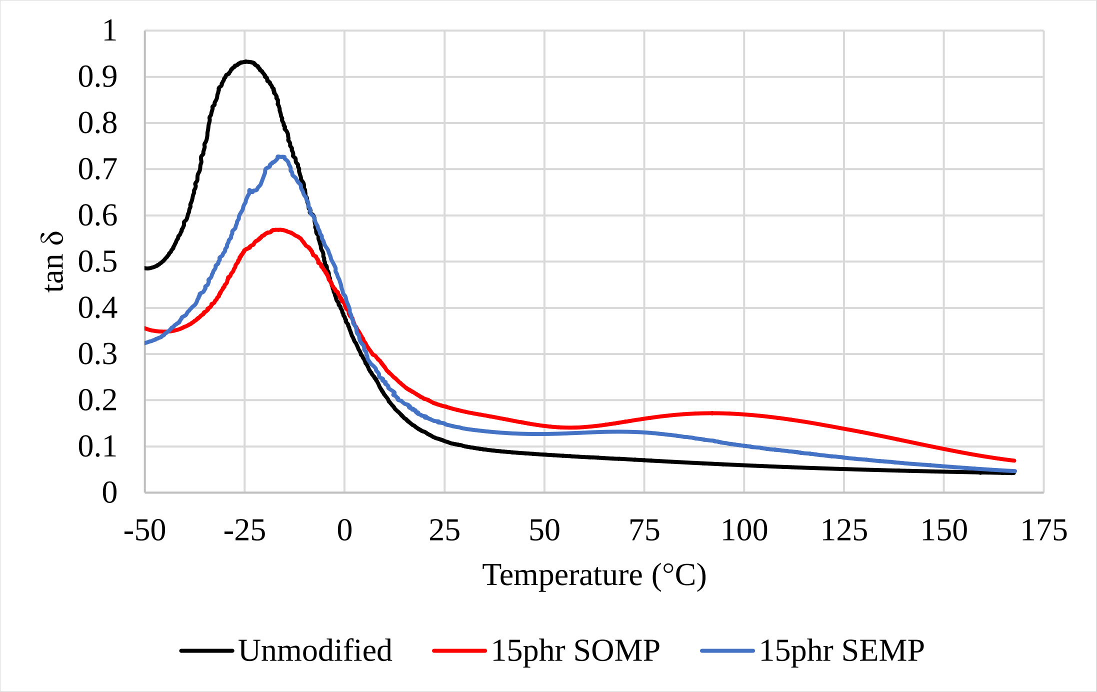


Figure 6. The figure above shows the temperature verse tan δ DMA curves for unmodified SBR, 15 phr SOMP in SBR, and 15 phr SEMP in SBR. From this data, one was able to calculate the glass transition temperatures of each rubber compound to be -25°C, -18°C, and -17°C respectively.

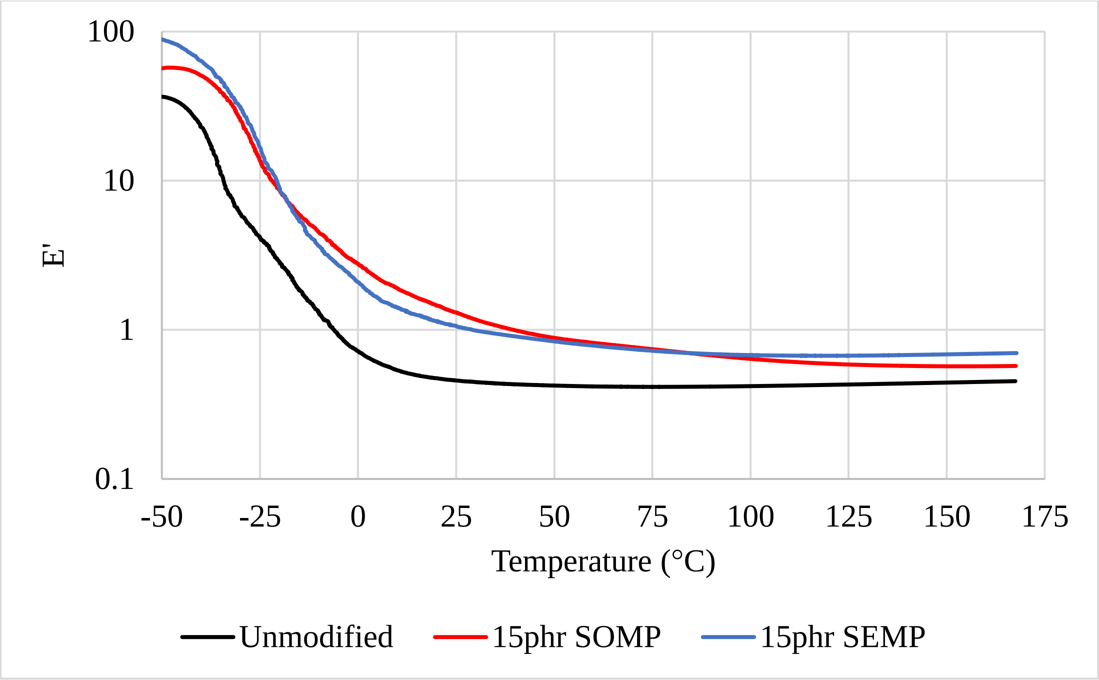


Figure 7. The figure above shows temperature vs storage modulus DMA curve for unmodified SBR, 15 phr SOMP in SBR, and 15 phr SEMP in SBR. From observation of the graph there is no transition to a secondary plateau modulus.

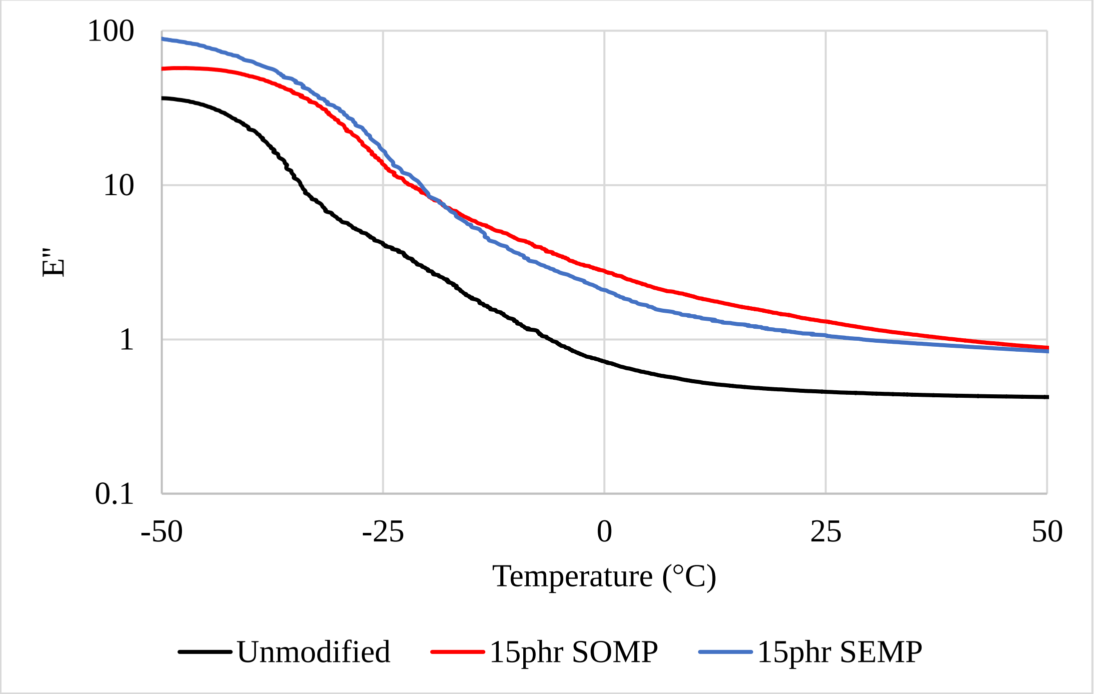


Figure 8. The figure above shows temperature vs loss modulus DMA curve for unmodified SBR, 15 phr SOMP in SBR, and 15 phr SEMP in SBR. From observation of the graph there is no transition to a secondary plateau modulus.

Extraction Tests

Table 2. The table below shows the calculated amount of extracted solids, oil in formulation, and SOMP in formulation.

SBR	**Extracted Solids (%)**	**Oil in Formulation (%)**	**SOMP in Formulation (%)**
5phr SOMP	20.4	20.0	3.8
15phr SOMP	19.3	18.6	10.6

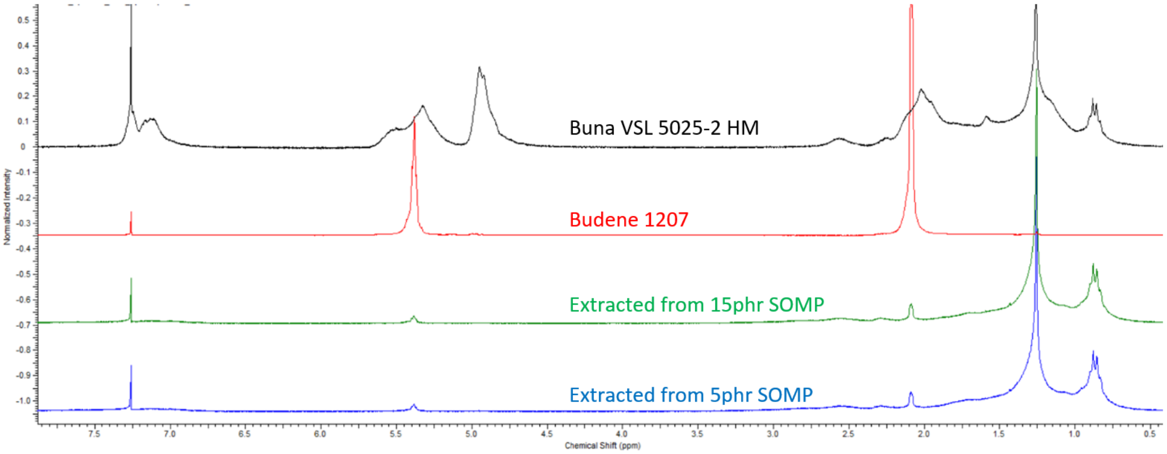


Figure 9. The above NMR graphs show a comparison between BUNA VSL 5025-2 HM, Bundane 1207, extract from 15 phr SOMP, and extract from 5 phr SOMP.

From **Table 2**, the amount of extracted solids is similar to that of oil in the formulation therefore concluded that it was mostly oil extracted from each rubber sample. To confirm NMR was taken of each extracted sample shown in **Fig. 9**. The only peaks that show in either extraction graph are the same peaks of that in the two rubber graphs and oil. This allows the conclusion that mostly oil was extracted from the two SOMP samples.

IR Spectra

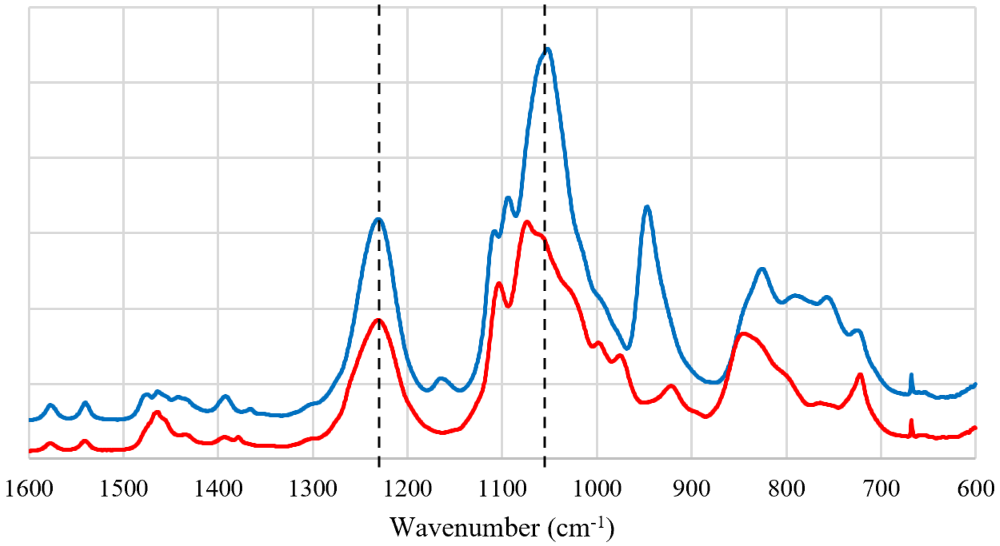


Figure 10. The graph above shows the IR spectra comparison between SEMP (blue) and SOMP (red) surfactants. There were two main peaks present in each spectrum located at 1237 cm^{-1} (α) and 1058 cm^{-1} (β).

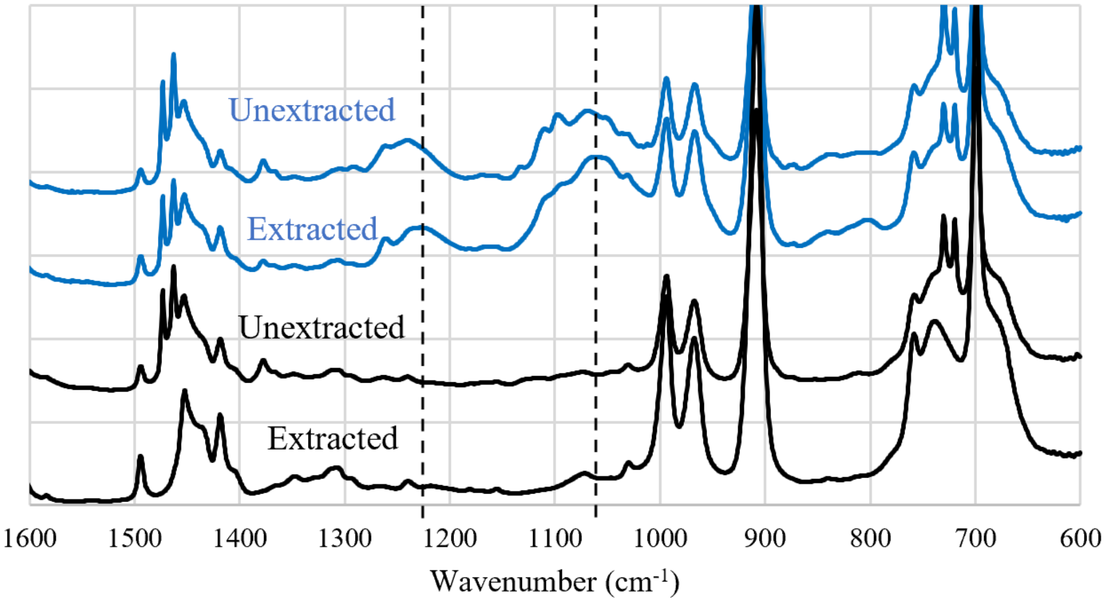


Figure 11. The graph above shows the IR spectra comparison between all SEMP concentrations. The black lines are 5 phr SEMP in SBR before and after extraction, while the blue lines are 15 phr SEMP in SBR before and after extraction.

From **Fig. 11**, at α and β, the samples before and after extraction show the approximately the same intensity of each peak showing that the surfactant does not get extracted. The surfactant, SEMP, is grafted to the rubber using the thiolene reaction which then associate to form physical crosslinking. This result shows that some of the phosphate diester remains in the rubber after extraction.

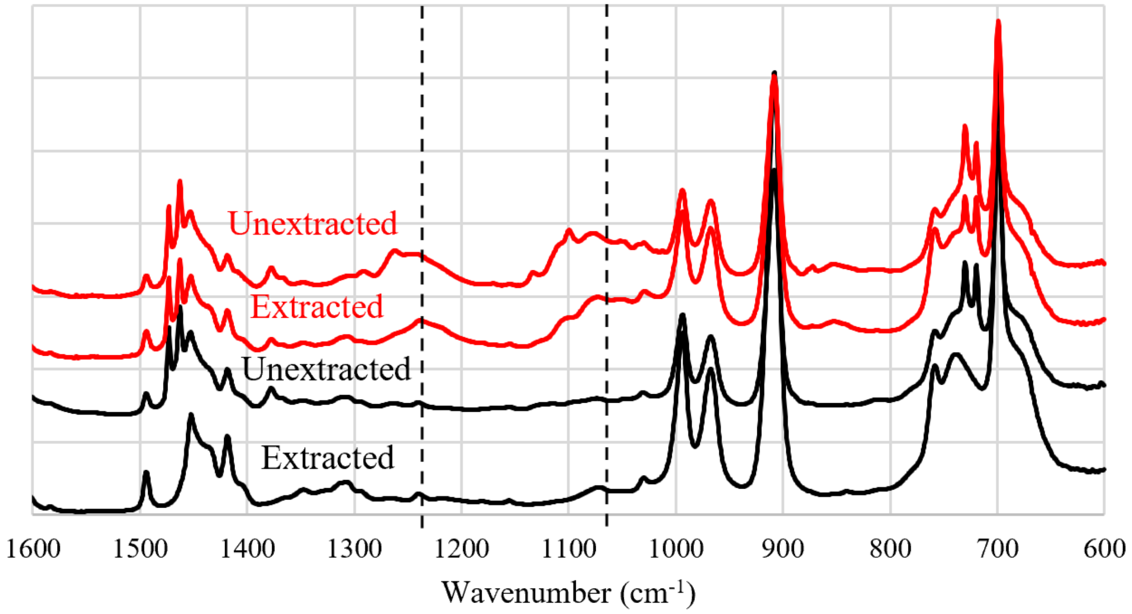


Figure 12. The graph above shows the IR spectra comparison between all SOMP concentrations. The black lines are 5 phr SOMP in SBR before and after extraction, while the red lines are 15 phr SOMP in SBR before and after extraction.

From **Fig. 12**, at α and β, the samples before and after extraction show the approximately the same intensity of each peak showing that the surfactant does not get extracted. The surfactant, SOMP, is grafted to the rubber using the thiolene reaction which then associate to form physical crosslinking. This result shows that some of the phosphate diester remains in the rubber after extraction.

Stress Relaxation

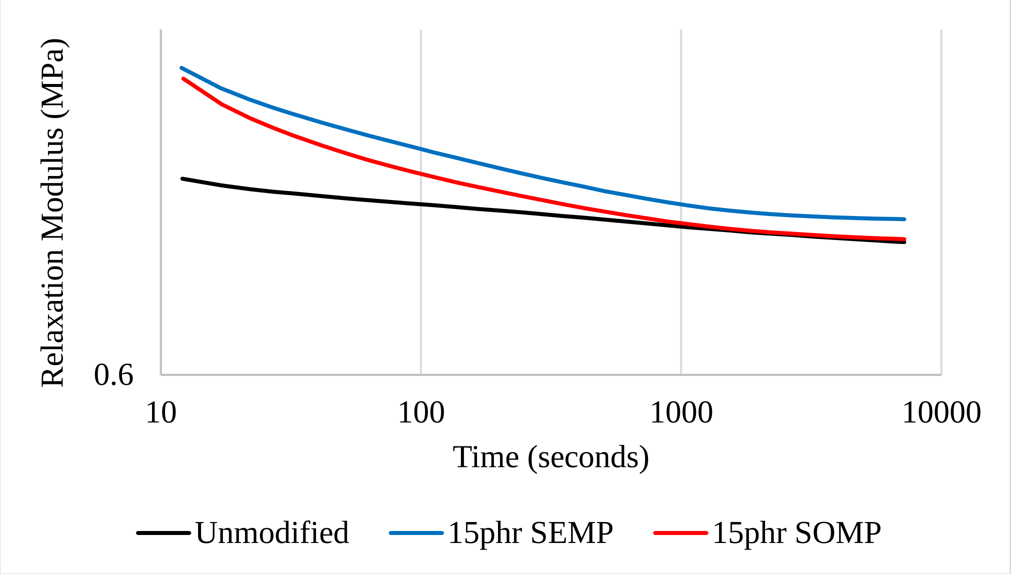


Figure 14. The graph above shows the relaxation modulus for unmodified SBR, solidified 15 phr SEMP, and solidified 15 phr SOMP.

From **Fig. 14** above, one can see the relaxation modulus of the modified rubbers are greater than the unmodified SBR sample. The relation modulus was used to calculated molecular weight between crosslinks of each sample. The molecular weight between crosslinks of the unmodified sample was the highest at 8834 g/mol. The SOMP samples had the second highest molecular weight between crosslinks at 8762 g/mol. The SEMP samples had the lowest molecular weight between crosslinks at 8283 g/mol.

Conclusion and Recommendations

It was found throughout this testing that SEMP and SOMP can be physically crosslinked with SBR to create a mechanically stronger piece of rubber than unmodified SBR. The modified rubber can have numerous commercially viable outcomes such as tires, gloves, etc. due to the added strength without the addition of other crosslinking agents. More research needs to be pursued in this area to find the optimum concentration of each surfactant while mixed in rubber. Blends of these two surfactants could also be considered. Other ionic compounds can be investigated in hopes of better physical crosslinking and ease of use small scale and eventually large scale.

Acknowledgements

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Work Cited

Qian, M. (2018). Reinforcement of Elastomers by Reactive Ionic Surfactant Filler [Master's thesis, University of Akron]. OhioLINK Electronic Theses and Dissertations Center. http://rave.ohiolink.edu/etdc/view?acc_num=akron1522424439025308