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Reprocessable and Easy Processing Silica Filled Brominated Isobutylene para Methyl Styrene (BIMS)

Wai Keung Wong

ExxonMobil Chemical Europe, Hermeslaan 2, B1831 Machelen, Belgium
E-mail: john.k.wong@exxonmobil.com

Summary: Without the use of any curatives, silica filled BIMS compounds can achieve tensile strength and bound rubber level close to conventional crosslinked elastomer compounds. This outstanding tensile performance of silica filled BIMS compounds results from the strong interaction between BIMS polymer and silica filler. Silica filled BIMS compounds can be reprocessed and still retain their high tensile strength performance. The good compatibility between BIMS and silica also leads to better filler dispersion and inhibition of filler-filler interaction. This in turn leads to the lower processing viscosity observed. We speculate that BIMS can interact with silica via nucleophilic substitution reaction between benzylic bromide of the polymer and surface silanol group of silica.

Keywords: BIMS; interaction; processing; reprocessability; silica

Introduction

In industrial applications, elastomers are typically compounded with various particulate fillers such as carbon black, silica, silicate, clay etc. [1-6] Most of these fillers act as reinforcement to the polymer matrix and can also reduce compound cost.

In comparison to carbon black, silica filled elastomers can provide certain performance advantage such as tear strength. However, silica filler is more difficult to disperse in non-polar elastomers and requires special silane coupling agent and mixing conditions for effective incorporation. Despite the above, there is a recent surge of interest in using silica as filler. This is because silica filled elastomers can provide low rolling resistance tread composition and offer a better balance of traction and treadwear in comparison to carbon black filled elastomer [7].

Silica generally has a higher tendency than carbon black to form filler-filler interaction in polymer matrix, leading to higher processing viscosity [4].

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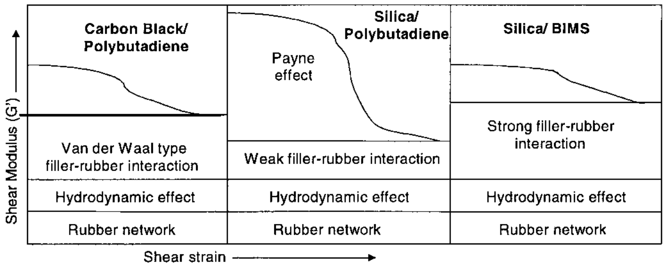

Figure 1. Schematic diagram showing the contribution factors of shear modulus in various filled compounds.

Figure 1 shows that silica filled polybutadiene has dramatically higher shear modulus (G') at low strain due to the presence of strong filler-filler interactions. This is known as the Payne effect [8, 9]. At high strain amplitude, the filler-filler linkage breaks down by the dynamic straining and as a result a decrease in shear modulus is observed [10]. Carbon black filled polybutadiene and silica filled BIMS do not exhibit significant Payne effect indicating a reduction in filler-filler interaction.

There is little interaction between surface silanol groups of silica and non-polar polymer matrices. In order to overcome these drawbacks, mercapto silanes such as triethoxysilyl propyl tetrasulfane (Si69) that can react with silanol groups of silica (through ethoxyl) as well as the double bond in unsaturated elastomers (through tetrasulfane) have been developed and used by the industry [11]. These mercapto silanes also promote dispersion of silica in elastomers and reduce filler-filler interaction, leading to improved processability and better physical and dynamic performances of filled elastomer.

Experimental

All the compounds were mixed in the same manner using a 300cc Haake Rheomix with a minimum of 3 minutes mixing time at a constant temperature of 150°C to ensure optimal silanization reaction. Finalization was carried out using an open mill set at 60°C.

The bound rubber tests were carried out by first dissolving the samples in toluene at room temperature for 1 week. The solution was then filtered and any sample remaining on the filter was allowed to dry under vacuum at 80°C for 3 days or until the weight becomes constant. The % bound rubber of sample is calculated using the equation:

Bound rubber (%) = [(wt of dried sample remain on filter - wt of filler in the sample) X 100] / (wt of polymer in the sample) (1)

Results and Discussion

Figure 2 shows the Mooney viscosity change with temperature of BIMS (Exxpro 3745) (note: Exxpro is the trade name of BIMS) and polybutadiene (Budene 1207, PD) as well as N660 black or high dispersion silica (Zeopol 8745) filled compound. All compound contains 50 phr filler (when present), 20 phr of oil, 3 phr of Si69 (when present) and curing agents. It can be observed that silica filled polybutadiene exhibits much higher Mooney viscosity than silica filled Exxpo 3745 compound. This is attributed to the extensive silica network formation in the silica filled polybutadiene compound [12, 13].

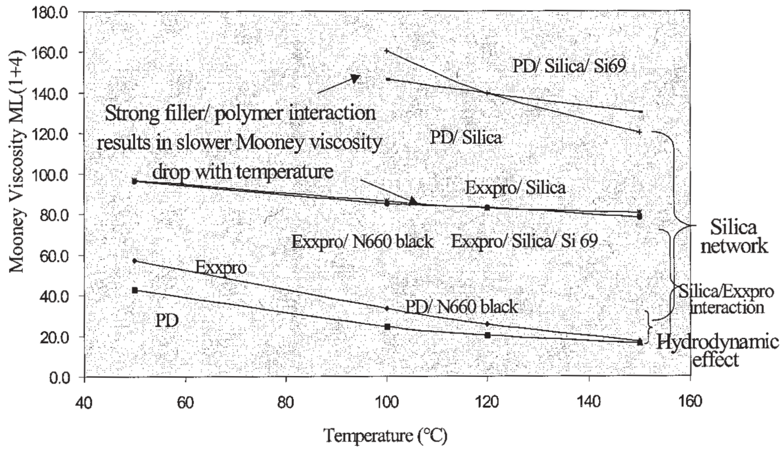

Figure 2. Mooney viscosity versus temperature plot of carbon black and silica filled model compounds.

It can also be observed that the rate of decrease of Mooney viscosity with temperature for silica filled polybutadiene is significantly less when Si69 is present. This is because Si69 promotes strong interactions between silica and polybutadiene and therefore rendering the compound more resistant to flow. The rate of decrease of Mooney viscosity with temperature for silica filled Exxpro 3745, with or without Si69, is similar to that of silica filled polybutadiene that contains Si69. This indicates that BIMS can promote good interaction with silica and minimize silica network formation even without silane.

The amount of bound rubber of silica (Zeopol 8745) and carbon black (FEF N220) filled model compounds that consist of only polymer, filler and in some cases Si69 have been determined and shown in Figure 3.

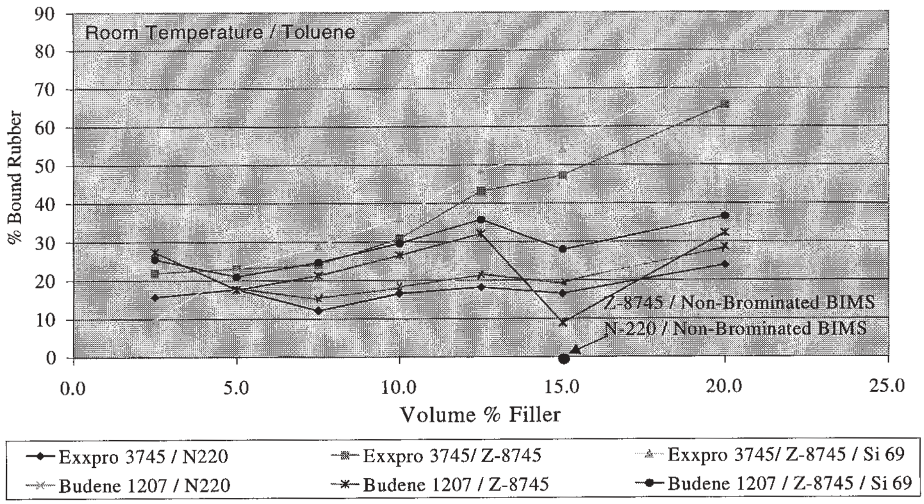

Figure 3. Bound rubber level of silica and carbon black filled model compound.

It can be observed that silica has much higher affinity to BIMS than to polybutadiene while carbon black exhibits similar affinity to both polymers. It can also be concluded that benzylic bromide is responsible for the high bound rubber level observed in silica filled BIMS. Non-brominated BIMS has zero bound rubber for both silica and carbon black filled samples. The much higher bound rubber level of silica filled BIMS compound in comparison to the carbon black filled one further confirms the existence of good interactions between BIMS and silica.

Table 1 compares the tensile performances of silica filled polybutadiene (PD) and Exxpro 3745 to that of crosslinked elastomer compounds.

Table 1. Mooney viscosity and tensile properties of silica filled compounds.

Tensile bar molding conditions		**180°C for 20 minutes**		
	Mooney Viscosity ML 1+4 (100°C)	100% Modulus (MPa)	Max. Tensile Strength (MPa)	Elongation at break (%)
PD/ silica	>200	1.6	3.0	270
PD/ silica/ Si69	>200	1.5	2.4	270
Exxpro/ silica	139	2.8	4.4	325
Exxpro/ silica/ Si69	130	3.6	8.1	295
Crosslinked EPDM hose compound	-	3.2	10.5	400
Crosslinked Bromobutyl innerliner compound	-	0.8	9.1	895

All the silica filled, non-crosslinked polybutadiene and BIMS compounds contain 20 volume % filler and 3.3 phr of Si69 (if present) without any oil or curing agent. It can be observed that the silica filled BIMS compound has much lower Mooney viscosity in comparison to the silica filled polybutadiene. Furthermore, tensile properties similar to crosslinked elastomer compounds can be achieved for the silica filled BIMS compound. It can also be observed that the use of Si69 further enhances tensile properties of silica filled BIMS but has no effect on silica filled polybutadiene. This indicates that the incorporation of Si69 leads to further improvemnt of silica reinforcement of BIMS. Si69, bound to the silica surfaces, promotes interaction between unsaturated polymer and silica via reaction of the tretasulfane with unsaturations [4]. Since BIMS polymer contains no unsaturation and crosslinking is via Friedel-Crafts mechanism [14] rather than via radical or ionic reactions that involves sulphur, the mercapto functional group of Si69 is unlikely to be involved in the interaction between silica and BIMS. It has also been shown that sulphur has no effect on the crosslinking of BIMS [15]. The enhancement of tensile properties observed due to the presence of Si69 most likely results from a nucleophilic substitution reaction between benzylic bromide of BIMS and surface silanol group of silica:

$$\underset{H}{Si\text{-}O^-} + Br\text{-}CH_2\text{-}PH \rightarrow \underset{H}{Si\text{-}O}\text{-}CH_2\text{-}PH + Br^-;$$

where PH stands for phenyl group.

This type of well known displacement reaction is best exemplified by the conversion of an alkyl halide into an alcohol by aqueous base:

$$HO^- + R\text{-}Hal \rightarrow HO\text{-}R + Hal^-;$$

where Hal stands for halogen such as Br, Cl, I.

Therefore the role of the silane coupling agent (Si69) is simply to further improve silica dispersion and therefore exposes more filler surfaces for interacting with BIMS. This is illustrated in Table 2 which shows that a variety of silane coupling agents, irrespective of their functional group, can further enhance the physical performances of silica filled BIMS (Exxpro 3745).

Table 2. Effect of silane coupling agents on tensile properties of silica filled Exxpro 3745 compounds.

Tensile bar molding conditions		180°C for 20 minutes		
All compounds contain 20 vol % filler without any curing agent or oil	Mooney Viscosity ML 1+4 (100°C)	100% Modulus (MPa)	Max. Tensile Strength (MPa)	Elongation at break (%)
No silane				
No silane	139	2.8	4.4	325
Alkyl silane				
PTMO (0.5)	139	2.9	5.6	350
PTEO (1.2)	138	2.5	5.7	400
A1630 (1.6)	>200	3.0	7.3	280
Mercapto silane				
Si69 (3.3)	130	3.6	8.1	295
MTMO (1.5)	125	3.3	5.1	320
Methacrylate silane				
Y11878 (1.6)	137	2.5	5.1	415
Amino silane				
AMMO (2.2)	141	3.6	5.2	260

The silane coupling agents listed in Table 2 are:

PTMO: n-propyl trimethoxysilane

PTEO : n propyl triethoxysilane

A1630: n-methyl trimethoxysilane

Si69: Bis(3-triethoxysilylpropyl)tetrasulfane

MTMO: 3-mercaptropropyl trimethoxysilane

Y11878: γ-methacryloxypropyl triethoxysilane

AMMO: 3-aminopropyl trimethoxysilane

Note: Numbers in brackets represent parts per hundred (phr) silane relative to the polymer

The above tends to suggest that the high tensile strength performances and high bound rubber level of silica filled BIMS is achieved mainly via strong interaction between filler and polymer. Table 3 shows that the silica-BIMS interaction does not lead to a three-dimensional crosslink network structure formation in the compound. Unlike conventional crosslinked rubber, silica filled BIMS can be remilled for 5 minutes using an open mill set at 120°C and then remolded under the same conditions (180°C for 20 minutes) and still retain their high tensile properties.

Table 3. Mooney viscosity and tensile properties of silica filled Exxpro 3745 compounds before and after remoulding.

Tensile bar molding conditions		180°C for 20 minutes		
All compounds contain 20 vol % filler without any curing agent or oil	Mooney Viscosity ML 1+4 (100°C)	100% Modulus (MPa)	Max. Tensile Strength (MPa)	Elongation at break (%)
Exxpro/ Silica	139	2.8	4.4	325
Remilled/ remolded	146	-	-	-
Exxpro/ Silica/ Si69 (1.5)	139	3.3	8.2	315
Remilled/ remolded	147	2.6	7.5	360
Exxpro/ Silica/ Si69 (3.3)	130	3.6	8.1	295
Remilled/ remolded	159	2.8	7.9	270

Conclusions

In this paper it is demonstrated that compounds of silica filled **B**rominated **I**sobutylene para**M**ethyl **S**tyrene (BIMS) is easier to process, as indicated by the lower Mooney viscosity, than similar compounds based on unsaturated polymers such as polybutadiene. Furthermore, the use of unconventional alkyl silanes can further improve processability as well as physical properties of silica filled BIMS while the same silanes have no effect on silica filled polybutadiene. Without the use of any curatives, silica filled BIMS compounds can achieve tensile strength and bound rubber level close to conventional crosslinked elastomer compounds. This outstanding tensile performance of silica filled BIMS compounds results from the strong interaction between BIMS polymer and silica filler instead of the crosslinking of polymer matrix. Furthermore, silica filled BIMS compounds that exhibit tensile strength of 8 MPa and elongation to break of around 300%, as well as bound rubber level of 80%, can be reprocessed by roll milling and still retain their physical performance after reprocessing. The good compatibility between BIMS and silica also leads to better filler dispersion and inhibition of filler-filler interaction. This in turn leads to lower processing viscosity. We speculate that BIMS can interact with silica via substitution reaction between benzylic bromide of the polymer and surface silanol group of silica.

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