Filler-Filler Interaction and Filler-Polymer Interaction in Carbon Black and Silica Filled Exxpro^{TM} Polymer

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Summary: Due to the presence of reactive benzylic bromide, Exxpro has much better interaction with silica in comparison with polybutadiene as demonstrated by the high bound rubber level. The better silica/Exxpro interaction is further substantiated by the low degree of filler network formation in comparison to that observed for silica filled polybutadiene as demonstrated by the much smaller deviation of low strain shear modulus from the Guth-Gold relationship for the silica filled Exxpro. Silane treatement of silica reduces filler network formation in polybutadiene but has only slight effect on silica filled Exxpro indicating that even without silane treatment silica already disperse well in Exxpro due to high degree of filler/polymer interaction. This result in silica filled Exxpro compound exhibiting better processability (lower shear viscosity) as well as dynamic performances for tire applications (higher tan δ at -20 and 0°C, lower tan δ at 60°C). We speculate that nucleophilic substitution reaction takes place between benzylic bromide and surface hydroxide group of silica.

Introduction

In industrial applications, elastomers are typically compounded with various particulate fillers such as carbon black, silica, silicate, clay, etc. [1-10]. Most of these fillers act as reinforcement to the polymer matrix and can also reduce compound cost. Fine particulate filler increases the stiffness and strength of vulcanized elastomer. Without filler, the mechanical strength of vulcanized elastomer is too low for most industrial goods and tire applications. For obtaining the full reinforcing potential of any filler, it must not interfere with the curing of the elastomer and have strong interactions with the matrix.

The vulcanized rubber surrounding filler particles can be considered as an isotropic elastic continuum with the same elastic properties as the rubber without filler. Equation 1 gives the dependence of small deformation Young's modulus (E) on the volume concentration (c) of filler:

$$E = E_0\,(1+2.5c + 14.1c^2) \qquad (1)$$

where E_0 is Young's Modulus of the matrix. This equation agrees well with the experimental data [4] plotted in Figure 1.

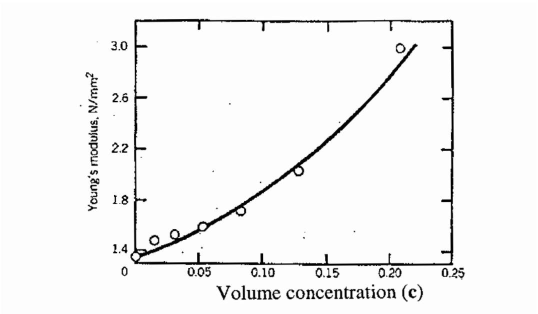


Figure 1. Young's Modulus, E, of an elastomer containing MT carbon black as a function of concentration, c. Equation (1) is represented by the curve.

The polymer at close proximity to filler particles, however, behaves differently from the matrix and that some sort of interactions between filler particle and rubber usually exists. Without these interactions, filler particles will not be able to transfer any load and no reinforcement effect can be obtained. Study of reinforced elastomer is complicated by the state of dispersion, e.g. filler network formation [11,12], and the disagglomeration of the agglomerated structure of filler particles with increasing dynamic strain amplitude [13]. There is still no consensus as to whether direct contact between filler aggregates is necessary for filler network formation [14]. Some work [15] points to the direction of polymer mediated filler network structure in filled Exxpro. Polymer chains that are at close proximity to filler surfaces lose their segment mobility and exhibit higher glass transition temperature, T_g (figure 2a). The Joint Rubber Shell model [16] (figure 2b) predicts that at temperature below the raised Tg of the joint shell rubber the 'trapped' polymer acts like a glass and cannot dissipate energy.

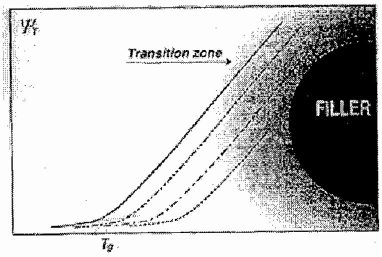


Figure 2a. The closer the polymer chain to the surface, the lower it's mobility (Ψ_T) and the higher the T_g.

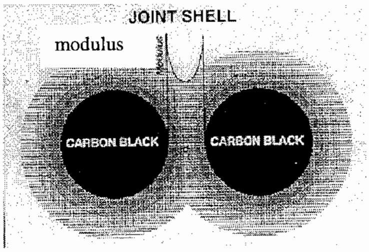


Figure 2b. At temperature close to the T_g of the joint rubber shell and trapped rubber, the polymer acts like a glass and cannot dissipate energy. Destruction of filler network releases the 'trapped' polymer and enables better energy dissipation.

Since coupling agent usually improves dispersion of filler in elastomers and therefore reduces the amount of 'trapped' polymer, use of coupling agent can bring about changes in the dynamic performance of filled elastomer compounds.

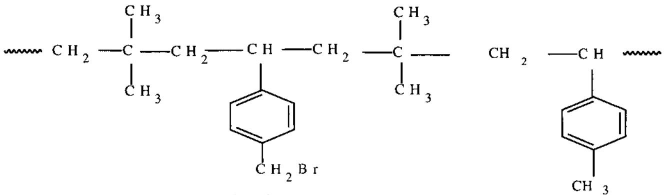
High state of filler dispersion should also lead to lower percolation threshold for filler network formation and therefore the compound becomes difficult to process even at low filler loading. However, if the coupling agent can prevent filler-filler interactions (e.g. silane coupling agent in silica filled elastomers) the high filler dispersion will not lead to 'effective' filler network that needs to be dissociated during processing.

The Filler

Furnace carbon black and precipitated silica are the most commonly used reinforcing fillers for elastomers. Carbon black contains various polar acidic oxygenated surface group that can interact with elastomers. It is generally agreed that interaction between carbon black and non-polar elastomer is physical (i.e. Van der Waal interaction) in nature [9]. Silica contains mainly surface silanol groups and the filler particles have higher tendency interacting amongst themselves via hydrogen bonding than with non-polar matrix [7]. In comparison to carbon black, silica filled compound has a higher tendency to form filler network in polymer matrix [7], leading to high processing viscosity. There is also little interaction between surface silanol group of silica and non-polar polymer matrix. In order to overcome these drawbacks, mercapto silanes such as triethoxysilylpropyl tetrasulfane that can react with silanol group of silica as well as double bond in unsaturated elastomers, such as polybutadiene, have been developed and used by the industry.

The Elastomer

Exxpro^{TM} polymer is a copolymer of isobutylene and para-methylstyrene that is subsequently brominated.



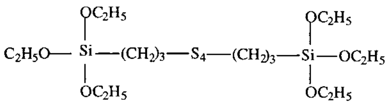
Brominated PMS
(0.5 -2 mole %)

PMS
(2 - 3 mole %)

Detailed characteristics and curing mechanisms of Exxpro have been reported previously [17].

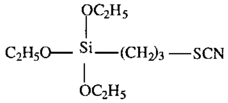
Mercapto Silane Coupling Agent

As mentioned in the filler section, mercapto silane coupling agents are used to minimize silica-silica interaction and to promote chemical linkage between silica and unsaturated elastomers. The ones that are most widely used in the rubber industry are:



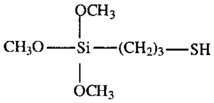
$$C_2H_5O-\underset{OC_2H_5}{\overset{OC_2H_5}{Si}}-(CH_2)_3-S_4-(CH_2)_3-\underset{OC_2H_5}{\overset{OC_2H_5}{Si}}-OC_2H_5$$

(TESPT - Si 69)
Bis (3-triethoxysilylpropyl) tetrasulfide



$$C_2H_5O-\underset{OC_2H_5}{\overset{OC_2H_5}{Si}}-(CH_2)_3-SCN$$

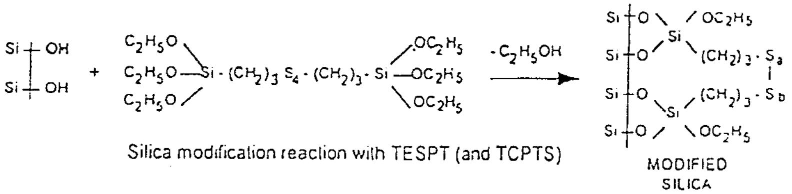
(TCPTS - Si 264)
3-thiocyanatopropyl triethoxysilane



$$CH_3O-\underset{OCH_3}{\overset{OCH_3}{Si}}-(CH_2)_3-SH$$

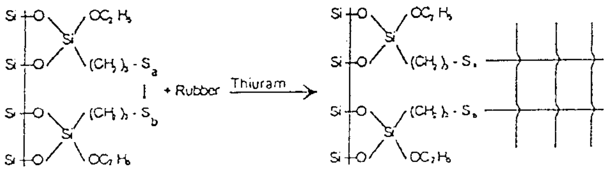
(MPTS - Si 189)
3- mercaptopropyl trimethoxysilane

The mechanism of how sulphide silane works is shown schematically below:



Silica modification reaction with TESPT (and TCPTS)

Bis (3-Triethoxysilylpropyl) tetrasulfide (TESPT) first reacts with surface silanol group of silica via condensation reaction to form Si-O-Si siloxane linkage. The hydrocarbon modified silica surface becomes much more compatible with elastomers. Silane modification of silica also greatly reduces adsorption of curatives by the filler. The sulphur group of the silane molecule can then participate in the sulphur crosslinking reation of unsaturated polymer such as polybutadiene.



Therefore, this type of silane coupling agent acts as a bridge chemically linking silica filler with unsaturated polymer. The use of silane coupling agent not only enhances silica reinforcement and reduces curative adsorption by silica but also improves silica dispersion in elastomer by reducing silica-silica interaction.

The main purpose of using bi-functional coupling agent in filled elastomer is to promote chemical linkage between filler and elastomer. However, care must be taken in choosing coupling agents (and indeed the filler itself) that they do not interfere with the elastomer vulcanization process. Study[18] has been made that show both carbon black and silica filler do not interfere with vulcanization (Friedel-Craft Alkylation reaction) of Exxpro.

Effect of silane coupling agent on the physical and dynamic performances of silica (Zeopol 8745) filled Exxpro

The physical and dynamic performances of 40 phr (parts per hundred with respect to the weight of elastomer) silica and carbon black filled Exxpro are listed in Table 1. All compounds contain 20 phr of paraffinic oil and cured using ZnO (2 phr), stearic acid (4 phr) and zinc dimethyldithiocarbamate (2.5 phr). All compounds were mixed in the same manner using a Haake internal mixer with a minimum period of 3 minutes mixing at a constant temperature of 150°C to ensure optimal silanization reaction. Finalization was carried out using an open mill at 100°C.

Table 1. Physical and dynamic performances of silica and carbon black filled Exxpro.

	No filler	N220	N660	Zeopol	Zeopol + 3phrSi 69	Zeopol + 1phrSi189	Zeopol + 1.5phrSi 264
ML (dNm)	0.5	1.3	0.9	1.8	1.4	2.3	1.3
MH (dNm)	2.7	7.0	5.1	6.2	6.3	8.3	6.3
MH-ML (dNm)	2.2	5.7	4.2	4.4	4.9	6.0	5.0
Mod 100% (Mpa)	0.4	1.6	1.0	0.9	1.0	1.5	0.9
Mod 300% (Mpa)	0.8	7.7	4.6	2.2	5.0	8.0	4.0
Mod 300%/Mod 100 %	2.0	4.8	4.6	2.4	5.0	5.3	4.4
Tensile (Mpa)	1.3	11.2	9.4	12.3	10.0	8.7	12.3
Elongation(%)	460	420	540	765	465	315	595
Mooney viscosity (100°C)	33	50	45	76	68	76	65
Hardness (Shore A)	23	50	42	40	41	43	38
Tan Delta (-20 °C)	1.55	0.96	1.2	0.92	1.12	1.17	1.05
Tan Delta (0 °C)	1.15	0.77	0.94	0.66	0.86	0.86	0.76
Tan Delta (60 °C)	0.59	0.17	0.16	0.14	0.1	0.06	0.11

It can be observed that the use of mercapto silane coupling agent increases significantly the modulus and reduces the elongation at break of silica filled Exxpro. This indicates that the silane coupling agent is providing some sort of interaction between Exxpro and silica. Furthermore, the use of these silane coupling agents increases significantly the tan δ of the compound at low temperatures (-20°C and 0°C) and reduces the tan δ of the compound at high temperature (60°C).

At temperature close to the raised T_g of the 'trapped' polymer, the release of 'trapped' polymer due to improved filler dispersion in the matrix will lead to an increase in the loss modulus, G", and hence tan δ of the compound. If the coupling agent also provides filler-matrix interaction and the strength of this interaction can be maintained at high temperatures, use of the coupling agent can lead to an increase in the storage modulus, G', and hence a reduction of tan δ of the compound at elevated temperatures. The dynamic property changes mentioned above favor tire performance requirements (i.e. high dissipation energy at low temperature for wet skid resistance and high elasticity at elevated temperature for low rolling resistance).

DMTA study on model compounds of silica filled Exxpro

Figure 3 compares the plots of G'_f / G'_{gum} versus filler loading of filled Exxpro and filled Budene (98% cis-polybutadiene) polymer and their deviation from the Guth-Gold relationship, which is based on the hydrodynamic effect and mutual disturbance caused by spherical particles [19, 20].

$$G'_f = G'_{gum}\,(1+2.5\varnothing+14.1\varnothing^2) \qquad (2)$$

Where G'_f and G'_{gum} are the shear moduli (at low strain) of filled compound and gum respectively, and $\varnothing$ is the volume fraction of the filler.

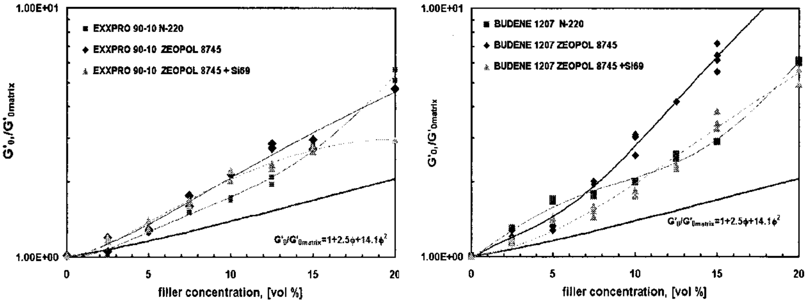


Figure 3. Plots of ratio of shear modulus of model compounds and matrix at low strain, $G'_0/G'_{0\ matrix}$, versus volume % filler concentration.

In comparison with silica filled polybutadiene, the much smaller deviation from the Guth-Gold relationship for silica filled Exxpro indicates less pronounced filler network formation. On the other hand, carbon black deviates similarly from the Guth-Gold relationship whether the matrix is Exxpro or polybutadiene. The low percolation threshold (at around 5 vol %) for filler network formation in Exxpro observed here is in agreement with that reported by Krishnamoorti, Tse et.al.[15]. The plots in Figure 3 also indicates that silane treatment of silica dramatically reduces filler network formation in silica filled Budene but has only slight effect on silica filled Exxpro when filler concentration is below 20 vol %. This may indicate that even without silane treatment, silica disperses well in Exxpro as a result of interaction between silica and Exxpro. Only at high filler loading level when the amount of Si-OH group outnumbers the benzylic bromide can the effect of silane in reducing filler-filler interaction through hydrogen bonding observed.

Effect of benzylic bromide on silica/Exxpro interaction

DMTA study on silica filled Exxpro model compounds reveal that the on-set of non-linearity of shear modulus, G', decreases progressively from about 6% strain to 0.3 % strain when filler loading increases from 2.5 volume % to 20 volume %, indicating the progressive influence of filler network as filler loading increases.

Figure 4 below shows the relationship between G'_{NORM} (G' of filled compound / G' of matrix) of 15 vol % silica filled Exxpro and the % strain of shear deformation.

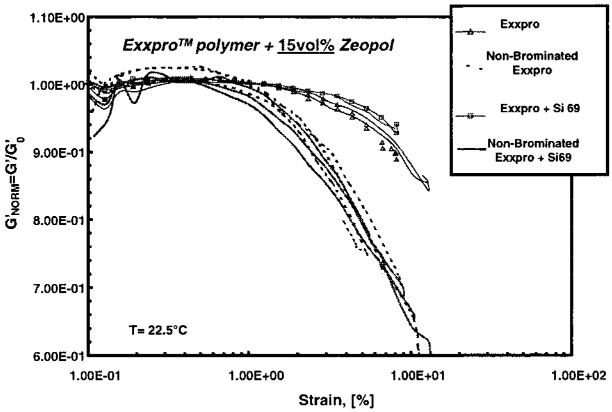


Figure 4. Plot of G' (filled compound)/ G' (matrix) versus shear deformation strain of 15 vol % silica filled Exxpro and non-brominated Exxpro.

When no benzylic bromide is present in the polymer, silica filled Exxpro deviates from the linear viscoelastic limit at much lower strain indicating high degree of filler network formation. Benzylic bromide promotes silica/Exxpro interaction and results in lower level of filler-filler interaction or network formation.

Bound Rubber

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 5.

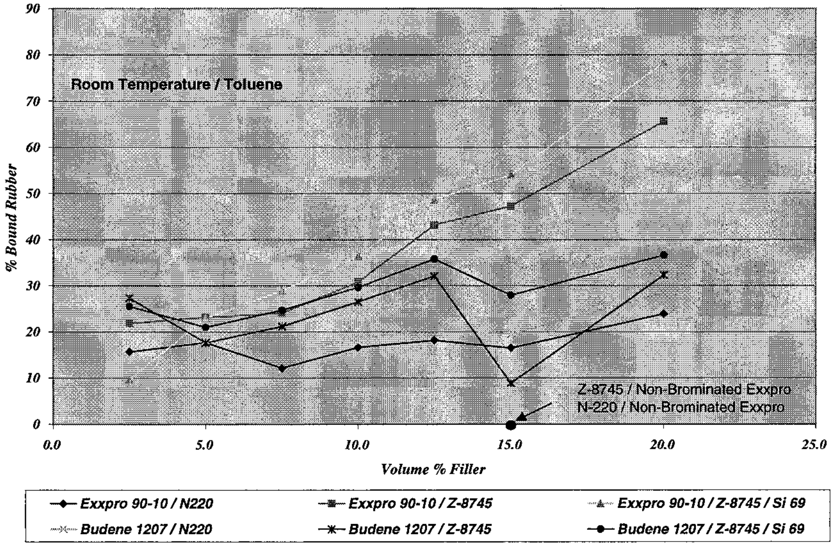


Figure 5. Bound rubber content of silica and carbon black filled model compounds.

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 remains 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) (3)

It can be observed that silica has much higher affinity to Exxpro than to Budene while carbon black exhibits similar affinity to both polymers. It can also be concluded that the benzylic bromide is responsible for the high bound rubber level observed in silica filled Exxpro. Non-brominated Exxpro has zero bound rubber for both silica and carbon black filled samples. We speculate that some sort of nucleophilic substitution reaction can take place between benzylic bromide and the surface hydroxide group of silica.

Conclusion

Due to the presence of reactive benzylic bromide, Exxpro has much better interaction with silica in comparison with polybutadiene as demonstrated by the high bound rubber level. The better silica/Exxpro interaction is further substantiated by the low degree of filler network formation in comparison to that observed for silica filled polybutadiene. Silane treatement of silica dramatically reduces filler network formation in silica filled polybutadiene but has only slight effect on silica filled Exxpro. This indicates that even without silane treatment silica disperses well in Exxpro due the higher degree of silica/Exxpro interaction. The high level of filler interaction enables silica filled Exxpro compound to exhibit better processability (lower shear viscosity) as well as dynamic performances for tire applications (higher tan δ at -20 and 0°C, lower tan δ at 60°C). We speculate that nucleophilic substitution reaction probably takes place between benzylic bromide and surface hydroxide group of silica.

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