Rheological Properties of Carbon Black/Silica Hybrid Filler in Acrylonitrile Butadiene Rubber

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Abstract. Filler is a common additive added into rubber vulcanizate to achieve reinforcing performance. Typically, filler is compounded via two-roll mill which results in filler agglomeration and lower reinforcing efficiency. To gain higher reinforcing efficiency, filler agglomeration must be minimized via masterbatch preparation. This study investigates colloidal stability of carbon black/silica (CB/SiO\(_2\)) hybrid filler and effectiveness between typical compounding and masterbatch process for NBR vulcanizate production. CB/ SiO\(_2\) hybrid filler was fixed at 20 wt.% with ratios of 100/0, 75/25, 50/50, 25/75 and 0/100 were dispersed separately in sodium hydroxide (NaOH) via ball milling. The zeta potential, particle size and viscosity results showed CB and SiO\(_2\) dispersions stabilized after 48 hours of ball milling. NBR masterbatch with 50/50 ratio has highest flow resistance. SiO\(_2\) reinforced NBR masterbatch showed higher flow resistance compared to CB due to finer silica particle size. However, scorch and cure time for SiO\(_2\) reinforced NBR is slower than CB reinforced NBR as silica deactivate the accelerator. CB/SiO\(_2\) at 50/50 has highest Tmax and ΔT while 100/0 and 0/100 has insignificant differences. As conclusion, CB and SiO\(_2\) dispersions were stable based on zeta potential analysis and particle size reduced as ball milling time increased.

1. Introduction
Acrylonitrile butadiene rubber (NBR) is a synthetic rubber with good elongation properties, adequate tensile strength and resistant to oil.\(^[1]\) Its properties affected by acrylonitrile and butadiene ratio. Increasing acrylonitrile content in NBR increase its polarity and transition glass temperature (\(T_{g}\)).\(^[2]\)

NBR is reinforced by filler e.g., silica (SiO\(_2\)) and carbon black (CB).\(^[3]\) SiO\(_2\) is a polar filler while CB is a non-polar filler.\(^[4]\) Lower filler’s structure gives better load sharing within rubber vulcanizate thus having better reinforcement.\(^[5]\) Typically filled compound is compounded via two-roll mill which results in filler agglomeration.\(^[6]\) The agglomerated filler results in lower reinforcing efficiency. Thus, to gain higher reinforcing efficiency, filler agglomeration must be minimized.\(^[7]\)

This can be achieved via masterbatch preparation; filler is dispersed in a selected medium before it is mixed with the latex. Thus, the colloid stability of the dispersed filler plays an important role.\(^[8]\) The colloid stability depends on its particle size, total potential energy (sum of repulsive and attractive force), diffuse electrical double layers (surface charge) and polarity.\(^[9]\) Deyaguin-Landau-Verwey-Overbeek (DLVO) theory describes stability is attained when repulsive Coulomb force is greater than attractive Van der Waals force.\(^[10]\) The repulsive force determined by the magnitude of zeta potential from electrical double layers.\(^[11]\)

NBR latex is a polar rubber thus poor dispersion with non-polar filler such as CB may exist and create poor reinforcement.\(^[12]\) Dispersing SiO\(_2\) in NBR latex is also challenging as both the filler and latex are polar.\(^[13]\) The aim of this study is to investigate the zeta potential, particle size and
viscosity of SiO₂ and CB dispersion for colloid stability. The cure characteristics of CB/SiO₂ filled NBR masterbatch also will be studied.

2. Experimental

2.1. Material

Table 1 shows the raw materials used in this study and its respective manufacturer.

| Material                  | Manufacturer                                |
|---------------------------|---------------------------------------------|
| Silica                    | Evonik Industries, Germany                  |
| Carbon black              | Cabot (M) Sdn. Bhd.                         |
| Nitrile butadiene latex   | Rivertex Technical Fabrics Group B.V.       |
| a) 6PPD                   | Flexys A.L.P.                               |
| b) TBzTD                  | Bayer (M) Sdn. Bhd.                         |
| c) TQ                     | Sovereign Chemical Company USA              |
| Zinc Oxide                | Bayer (M) Sdn. Bhd.                         |
| Stearic Acid              | Pacific Oleochemicals                       |
| Wax Antilux 654           | Rhein Chemie Rheinau Gmbh Germany           |
| Sulphur                   | Bayer (M) Sdn. Bhd.                         |

a) 6PPD: N-1,3-dimethylbutyl)-N-phenyl-p-phenylenediamine  
b) TBzTD: Tetrabenzylthiuram disulfide  
c) TQ: Polymerized 1,2 dihydro 2,2,4-trimethyl quinolone

2.2. CB and SiO₂ dispersions in NaOH

10 wt.% of CB and SiO₂ were dispersed in NaOH separately via ball mill machine (AMACO Model No. B, Serial No. C293) for 72 hours. Particle size and zeta potential of dispersion were analysed using zeta sizer (model: Brookhaven ZetaPlus) at ball milling time interval of 0.25, 0.5, 0.75, 1, 2, 3, 4, 5, 6, 24 and 72 hours.

2.3. CB and SiO₂ masterbatch

Based on particle size and zeta potential results, the ball milling time the CB and SiO₂ dispersions were fixed to 24 hours. These dispersions then mixed with NBR latex to form NBR mixtures according to CB/ SiO₂ ratio of 100/0, 75/25, 50/50, 25/75 and 0/100. The mixtures were coagulated to produce CB/ SiO₂ masterbatch using a microwave (Model: Electrolux EMM2001W) before oven dried (Model: Memmert) until constant weight.

2.4. Rubber compounding

The rubber compounding recipes summarizes in Table 2. Compounding was carried out using two-roll mill machine (Model: SLIMC SXK-160A).
Table 2. Formulations for rubber compounding

| Material \ Recipe           | 1  | 2  | 3  | 4  | 5  |
|----------------------------|----|----|----|----|----|
| Silica masterbatch         | 0  | 25 | 50 | 75 | 100|
| Carbon black masterbatch   | 100| 75 | 50 | 25 | 0  |
| 6PPD                       | 2.4| 2.4| 2.4| 2.4| 2.4|
| TBzTD                      | 1.0| 1.0| 1.0| 1.0| 1.0|
| TQ                         | 1.5| 1.5| 1.5| 1.5| 1.5|
| Zinc oxide                 | 3.5| 3.5| 3.5| 3.5| 3.5|
| Stearic acid               | 2.4| 2.4| 2.4| 2.4| 2.4|
| Wax antilux 654            | 1.0| 1.0| 1.0| 1.0| 1.0|
| Sulphur                    | 1.2| 1.2| 1.2| 1.2| 1.2|

2.5. Cure characteristics
Cure characteristics were carried out on all the filled rubber compounds. The test was performed using a rheometer (Model: Monsanto 100) according to ASTM D2084-93. The rheometer was set at 150 °C for 60 minutes with 12 g of sample.

3. Results and Discussion

3.1. Zeta potential and particle size
Fig. 1 and 2 show decreasing trend of particle size for CB and SiO₂ respectively. The increasing ball milling time will produce smaller particle size of filler. More time for mechanical treatment allows filler to be further reduced from larger into smaller size.[14] The magnitude of zeta potential increased (negative charge) as the ball milling time increased for both CB and SiO₂ dispersions. Alkaline dispersion medium such as NaOH gives negative value of zeta potential due to more hydroxyl groups.[15] Dispersion with zeta potential greater than or less than +30 mV or -30 mV respectively is a stable dispersion.[16]

![Fig. 1. Zeta potential and particle size of CB in NaOH dispersion](image)
Despite both CB and SiO$_2$ has their particle size decreased as the ball milling time increased, SiO$_2$ has smaller size compared to CB as showed in Fig. 3. SiO$_2$ most likely to have less aggregation formation due to polar hydroxyl group presents on its surface.[17] CB is non-polar thus attractive Van der Waals force may cause CB to form aggregates and affecting the mean particle size.[18]

3.2. **Viscosity**

Fig. 4 shows viscosity of both CB and SiO$_2$ dispersions decreased as the ball milling time increased. CB has bigger particle size most likely due to higher filler structure as compared to SiO$_2$. Higher magnitude of CB dispersion zeta potential suggested higher repulsive force among the CB particles. Therefore, due to the CB’s structure and its zeta potential, CB has higher viscosity.[19]
3.3. Cure characteristics

Cure characteristics of NBR masterbatches filled with CB/SiO$_2$ hybrid filler at different ratio (CB/SiO$_2$ of 100/0, 75/25, 50/50, 25/75 and 0/100) are shown in Table 3. Higher CB loading shorten both the scorch time and cure time of NBR masterbatch from 8.67 to 5.21 mins and 9.00 to 6.00 mins, respectively as incorporating more CB in rubber vulcanizate assist in vulcanization process.[20] Meanwhile, more SiO$_2$ results in longer scorch time and cure time of NBR masterbatches. It has hydroxyl group on the surface that may deactivate accelerator. Lower amount of sulfureting agent and actual accelerator making crosslinking to be slower and does affect the vulcanization process.[21]

| Characteristic     | 100/0 | 75/25 | 50/50 | 25/75 | 0/100 |
|--------------------|-------|-------|-------|-------|-------|
| Scorch time, $t_{s2}$ (min) | 5.21  | 6.11  | 6.72  | 6.25  | 8.67  |
| Cure time, $t_{90}$ (min)    | 6.00  | 7.00  | 7.00  | 7.00  | 9.00  |
| Minimum torque, $T_{min}$ (lb-in) | 11.25 | 10.35 | 15.10 | 15.08 | 13.20 |
| Maximum torque, $T_{max}$ (lb-in) | 54.91 | 56.73 | 72.10 | 49.10 | 55.70 |
| Delta torque, $\Delta T$ (lb-in)    | 43.66 | 46.38 | 57.04 | 34.98 | 42.50 |

100% filled NBR masterbatch with CB or SiO$_2$ has insignificant difference in $T_{max}$, $T_{min}$ and $\Delta T$ as shown in Fig. 5. The $T_{max}$, $T_{min}$ and $\Delta T$ has less than 5% difference between them. Loading of hybrid filler at 50/50 has the highest $T_{max}$ and $\Delta T$. Increasing CB loading does not have bigger influenced on $T_{min}$ of NBR masterbatch based on Fig. 5. Filled NBR compound with CB/SiO$_2$ ratio of 50/50 showed highest $T_{max}$ and $T_{min}$ which might due to the re-dispersion of both fillers.
4. Conclusion
Zeta potential shows both CB and SiO₂ dispersion were stable. The increasing ball milling time of CB and SiO₂ dispersion reduced the particle size. CB dispersion may have aggregation formation thus resulting higher particle size and viscosity compared to SiO₂ dispersion. Insignificant difference in T_max and ΔT between 100% CB and SiO₂ filled masterbatches. T_max and ΔT of hybrid fillers varies according to the ratio.

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