Nature of Carbon Black Reinforcement of Rubber: Perspective on the Original Polymer Nanocomposite

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# Speaker

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Introduction

• This presentation is based on our recent review paper
  – C.G. Robertson and N.J. Hardman, “Nature of Carbon Black Reinforcement of Rubber: Perspective on the Original Polymer Nanocomposite”, Polymers 13, 538 (2021), open access paper; link to free download: https://www.mdpi.com/2073-4360/13/4/538
  – Please see references cited therein (146 papers)
Introduction

Carbon Black
15 million metric tons per year

nano-scale reinforcement for demanding rubber applications

Endurica
MONOLITH

tires  non-tire rubber  inks, paints, plastics, etc.

20%
73%
7%
Introduction

- Adding carbon black (CB) particles to elastomeric polymers is essential to the successful industrial use of rubber in many applications.
- The mechanical reinforcing effect of CB in rubber has been studied for nearly 100 years.
- Despite these many decades of investigations, the origin of stiffness enhancement of elastomers from incorporating CB is still debated:
  - Purely physical adsorption of polymer chains on CB surfaces; or
  - Some polymer–particle chemical bonds are also introduced in the process of mixing and curing the CB-filled rubber compounds.
Introduction

• We review key experimental observations of rubber reinforced with CB, including the finding that heat treatment of CB can greatly reduce the filler reinforcement effect in rubber.

• The details of the particle morphology and surface chemistry are described to give insights into the nature of the CB–elastomer interfaces.

• We also discuss:
  – The influence of CB on crosslinking
  – Various chemical modification approaches that have been employed to improve polymer–filler interactions and reinforcement.
CB reinforcement of rubber

- A.I. Medalia and G. Kraus, 1994

![Graph showing stress-strain relationship with Reinforcement Index (RI)]
Reinforcement regions

Regions of Reinforcement
1. Payne effect
2. Minimum / transition
3. Stress upturn
4. Modulus plateau
5. Ultimate softening and break

\[ E = \frac{d\sigma}{d\varepsilon} \text{ (MPa)} \]

Strain (%)  
0 \quad 100 \quad 200 \quad 300 \quad 400 \quad 500

Stress (MPa)  
0 \quad 5 \quad 10 \quad 15 \quad 20 \quad 25
Reinforcement regions

- Data from N. Warasitthinon and C.G. Robertson, 2018
Reinforcement regions

- Data from N. Warasitthinon and C.G. Robertson, 2018
Reinforcement index to quantify stress upturn

• This new reinforcement index was introduced in our 2021 review paper
  \[ \kappa = \frac{E_{\text{plateau}}}{E_{\text{min}}} \]

• Many folks still use M300/M100
CB particle morphology

- N660 carbon black
CB structure and chemistry

- (b) adapted from R.D. Heidenreich, W.M. Hess, and L.L. Ban, 1968
Heat treatment of CB

Heat treatment of CB at 900 to 1200 °C removes surface functional groups without significantly affecting the surface area or graphitic structure.

Table 2. Effects of Heat Treatment on CB Characteristics.

| CB Sample         | NSA (m²/g) | STSA (m²/g) | O (%) | N (%) | H (%) | S (%) | C (%) | L_c (nm) | d_002 (nm) |
|-------------------|------------|-------------|-------|-------|-------|-------|-------|----------|------------|
| N234, untreated   | 126.4      | 120.3       | 2.21  | 0.145 | 0.337 | 0.924 | 93.7  | 1.19     | 0.365      |
| N234, 900 °C      | 134.7      | 124.7       | 1.28  | 0.158 | 0.250 | 0.932 | 95.9  | 1.15     | 0.361      |
| N234, 1000 °C     | 129.6      | 129.6       | 0.204 | 0.064 | 0.130 | 0.916 | 96.7  | 1.40     | 0.361      |
| N234, 1200 °C     | 129.0      | 132.8       | 0.128 | 0.041 | 0.021 | 0.790 | 98.7  | 1.44     | 0.355      |
| N660, untreated   | 36.4       | 35.2        | 0.576 | 0.082 | 0.339 | 1.84  | 95.9  | 1.78     | 0.352      |
| N660, 1000 °C     | 36.4       | 37.3        | 0.110 | 0.056 | 0.141 | 1.78  | 96.8  | 1.59     | 0.355      |

Data from Monolith Technical Center in Lincoln, NE. Heat treatment conditions: CB annealed in inert atmosphere under positive-pressure Ar flow at indicated temperature for 18 h. Elemental analysis results from Leco ONH836 and Leco SC832 Elemental Analyzers. Crystallographic data (L_c and d_002) from Rigaku Miniflex powder X-ray diffractometer utilizing k alpha radiation.
Heat treatment of CB

Table 4. Effects of CB Heat Treatment on Tensile Properties of CB-Filled SBR.

| CB Sample       | M100 (MPa) | M300 (MPa) | M300/M100 |
|-----------------|------------|------------|-----------|
| N234, untreated | 2.68       | 15.33      | 5.72      |
| N234, 900 °C    | 2.77       | 15.33      | 5.54      |
| N234, 1000 °C   | 2.11       | 11.11      | 5.27      |
| N234, 1200 °C   | 1.78       | 7.78       | 4.36      |
| N660, untreated | 2.59       | 13.33      | 5.15      |
| N660, 1000 °C   | 1.96       | 7.99       | 4.08      |

- N234 CB with surface functionality removed by heat treatment gives less reinforcement than untreated N660 CB
- Surface chemistry is more important than particle morphology

Data from Monolith Technical Center in Lincoln, NE (see Table 2 for CB characteristics). Heat treatment conditions: CB annealed in inert atmosphere under positive-pressure Ar flow at indicated temperature for 18 h. Results from room temperature tensile testing for emulsion SBR rubber formulation specified in ASTM D 3191.
Heat treatment of CB

E.M. Dannenberg, 1975

SBR + 50 phr ISAF CB (≈ N220)

Bound Rubber (%)

Bound rubber
M300

M300 (MPa)

CB Heat Treatment Temperature (°C)
Free radicals on CB

- G. Kraus and R.L. Collins, 1959
- R.L. Collins, M.D. Bell, and G. Kraus, 1960
Aggregate breakage during compounding

- M. Klüppel, 2003
Mixing time effect

- J.J. Brennan, T.E Jermyn, B.B Boonstra, 1964
Cure acceleration effect from CB

- S.M. Hosseini and M. Razzaghi-Kashani, 2018
Polymer-CB coupling

- Carbon black coupling agent
  - S. Han, W.-S. Kim, D.-Y. Mun, B. Ahn, and W. Kim, 2020

- Sn-functional groups on polymers have shown reaction with quinone groups on CB
  - V.A. Escobar Barrios and M. Garcia-Ramirez, 2003
  - F. Tsutsumi, M. Sakakibara, and N. Oshima, 1990
  - J.D. Ulmer, W.L. Hergenrother, and D.F. Lawson, 1998
Possible polymer–filler interaction/reaction scenarios

- Adsorption
- Adsorption + covalent bonding
- Covalent bonding

+ Crosslinking effect
Final Comments

• Heat treatment of CB at 900 to 1200 °C removes surface functional groups without significantly affecting the surface area or graphitic structure, and this greatly reduces the bound rubber and mechanical reinforcement.

• Considering the research literature in total, we believe that the most realistic scenario for polymer–CB interfaces is predominantly physical adsorption with some covalent chemical bonds also present.
Final Comments

• Additional complexities include:
  – Aggregate breakage during compounding
  – Free radical chemistry during compounding
  – Accelerating effect of CB on the sulfur vulcanization of rubber

• The cure acceleration effect may produce a layer around the particles with increased crosslink density compared to the bulk

• However, additional analytical research is needed since the exact nature of the polymer–filler interfaces in the final cured rubber has yet to be conclusively diagnosed
Acknowledgements

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Thank you for attending!