Aging Resistant Elastomer Reinforcement by Antioxidant Loaded Clay Nanotubes

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Abstract. An aging resistant styrene-butadiene rubber (SBR) composite was prepared by using N-isopropyl-N’-phenyl-p-phenylenediamine (antioxidant 4010NA) loaded halloysite nanotube (HNT) as filler. The antioxidant loaded in the tube lumens of HNTs allowed for sustained released through HNT openings, provided longer supply of antioxidant in rubber composite and enhanced the aging resistance of rubber. Surface modifying of HNTs with silane coupling agent was used to improve the performance of SBR/HNTs nanocomposites. The aging resistance of SBR/HNTs was studied by oxygen adsorption and heat aging method. The antioxidant loaded HNTs not only worked as fillers for better mechanical properties but also can be used for improving aging resistant.

1. Introduction
Halloysite nanotube (HNT) is an economically viable two-layered aluminosilicate with a predominantly hollow tubular structure in the submicron range. The size of halloysite particles varies within 1-1.5 μm in length and 10-15 nm of inner diameter. Due to its high aspect ratio (L/D ~ 30), it gives a large amount of filler-polymer interactions compared to spherical nanoparticles improving mechanical and thermal properties of the polymeric composites [1-4]. Loading these tube lumens with N-isopropyl-N’-phenyl-p-phenylenediamine (antioxidant 4010NA) and doping them at 30-50 % into styrene-butadiene rubber (SBR) allows for controlled sustained release halloysite nanotube openings, increasing the amount of antioxidant used in the rubber composite [5-8]. The sustained release of antioxidant can avoid the blooming caused by the high antioxidant content in rubber. Tight interfacial bonding and fine dispersion of the clay are two crucial factors to determine the performance of the SBR/HNTs nanocomposites, which can be achieved by surface modification of HNT with silane coupling agent. The aging resistance of SBR/HNTs was studied by oxygen adsorption and heat aging method [9-11].

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2. Results and Discussion

2.1 Loading procedures of Antioxidant

HNT (two times weight of antioxidant) was mixed thoroughly with antioxidant acetone solution (30 g/L) and placed in a vacuum chamber at 100 torr for 30 minutes then at standard atmosphere for 15 minutes. This vacuum cycle was repeated three times followed by washing and drying.

![Loading procedure of active agents into halloysite nanotube and (b) the formula of antioxidant 4010NA.](image)

**Fig. 1** (a) Loading procedure of active agents into halloysite nanotube and (b) the formula of antioxidant 4010NA.



![TGA curves of antioxidant 4010NA loaded HNTs](image)

**Fig. 2** TGA curves of antioxidant 4010NA loaded HNTs

The TGA curves of samples with different HNTs/antioxidant weight ratios are shown in Fig. 2. The loading efficiency calculated with the formula (I) is listed in Table 1. The loading efficiency increases with the decreasing of weight ratio of HNTs/4010NA until its maximum value.

\[ c_A = (1 - \frac{w_{H-A}}{w_H}) \times 100\% \]  

(1)

\( c_A \) - the loading efficiency of antioxidant

\( w_{H-A} \) - the weight of antioxidant loaded HNTs at 600°C

\( w_H \) - the weight of HNTs at 600°C

| HNTs/4010NA  | 4:1 | 2:1 | 1:1 | 1:2 |
|--------------|-----|-----|-----|-----|
| Loading efficiency | 0.8% | 1.5% | 3.8% | 8.1% |

2.2 Release of Antioxidant from HNT lumens

The release of antioxidant in cyclohexane is much faster than in water (Fig. 3), attributed to the higher solubility of antioxidant in cyclohexane. The large release amount at the initial stage is acceptable. For one reason is the release in rubber will be slowed down as the HNTs are coated with the cross-linked polymer, another is the aging resistant system of elastomer needs an initial concentration of antioxidant.
2.3 Preparation of the SBR/HNTs nanocomposites
SBR and HNTs were compounded with rubber additives with a two-roll mill at room temperature. The compound was press-cured to a 1-mm-thickness sheet at 170°C × Tc90 and then cut into specimens for measurements.

| Sample code | SBR | HNTs (phr) | HNTs/4010NA (phr) | 4010NA (phr) |
|-------------|-----|------------|------------------|--------------|
| SBR#1       | 100 | -          | -                | -            |
| SBR#2       | 100 | 40         | -                | -            |
| SBR#3       | 100 | -          | -                | 1.5          |
| SBR#4       | 100 | -          | 40               | -            |
| SBR#5       | 100 | -          | 40               | 1.5          |

a Rubber intergradients: zinc oxide, 5 phr; stearic acid, 1 phr; dicumyl peroxide (DCP), 1 phr.

2.4 Morphology and mechanical properties of SBR/HNTs nanocomposites
The morphology of SBR/HNTs nanocomposites is shown in Fig. 4. The dispersion of HNTs with silane coupling agent is much better and the majority of HNTs are embedded in the matrix. Table 3 shows the mechanical properties of SBR/HNTs nanocomposites before and after aging at 120°C for 24h and 72h. It is revealed that the overall mechanical properties are increased with silane coupling agent. That is because the organic layer brought on the HNT surface by silane decreases the surface energy and increases the dispersion of HNTs in SBR while enhancing the interaction between HNTs and rubber. After aging, less decrease of mechanical properties was performed by the antioxidant loaded HNTs reinforced SBR than the HNTs reinforced SBR with adding antioxidant directly while mixing. The sustained release of antioxidant makes it long-acting and avoids the blooming caused by the high antioxidant content in the nanocomposites.
Table 3 the mechanical properties of SBR/HNTs nanocomposites before and after aging

| Sample code | Ts/MPa | Eb/%  | Hardness (shore A) |
|-------------|--------|-------|--------------------|
| Before aging |        |       |                    |
| SBR#1       | 2.36   | 563   | 42                 |
| SBR#2       | 14.97  | 523   | 64                 |
| SBR#3       | 2.41   | 557   | 43                 |
| SBR#4       | 15.11  | 517   | 64                 |
| SBR#5       | 15.20  | 515   | 65                 |
| Changes after aging at 120°C×24h |        |       |                    |
| SBR#1       | -76%   | -48%  | +12                |
| SBR#2       | -70%   | -51%  | +12                |
| SBR#3       | -57%   | -31   | +8                 |
| SBR#4       | -60%   | -34%  | +10                |
| SBR#5       | -53%   | -27%  | +8                 |
| Changes after aging at 120°C×72h |        |       |                    |
| SBR#1       | -      | -55%  | +14                |
| SBR#2       | -      | -57%  | +14                |
| SBR#3       | -      | -36%  | +9                 |
| SBR#4       | -      | -39%  | +11                |
| SBR#5       | -      | -31%  | +9                 |

3. Conclusion
In this work, an aging resistant rubber nanocomposite was prepared by using antioxidant loaded HNTs as not only controlled sustained release of antioxidant but also fillers improved the mechanical properties of rubber composite. After 72 hrs aging at 120°C in oxygen atmosphere, halloysite-4010NA antioxidant rubber composites have shown ca. 31 % elasticity drop as compared with 55 % drop for unloaded rubber accomplished.

4. References
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