Effect of CNTs on Mechanical and Abrasion Properties of NBR

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Abstract. Mechanical properties, abrasion properties and morphology of CNTs/NBR were studied in this paper. The addition of carbon nanotubes can effectively improve the aging and wear resistance of rubber composites. SEM demonstrated that agglomeration phenomenon occurs when the content reaches 4phr.

1. Introduction

As chalcogenide materials, carbon nano tube (CNTs) has unique characteristic such as remarkable mechanical, thermal, and electrical properties in elastomer composites as nano filler. The research gap in synthesis and properties of carbon nanotubes along with development of CNTs/polymer was identified [1]. The net resistance of multi-wall carbon nanotubes (MWNTs) and the contact resistance between MWNTs and electrode have been determined by R.Enomoto et.al [2]. It was found that the high value of CNTs loading in the non-polar NR phase was explained by taking into consideration the presence of phospholipids [3]. Composite can deliver all the individual elemental property of the material. A small amount of the MWCNTs in rubber composites showed remarkable improvement in mechanical, thermal and electrical properties [4-7]. Segregated network of CNTs resulted in very low electrical percolation threshold (0.043vol %) for the composite with enhanced dielectric properties [5]. The upper limit of the temperature for continuous use of the fluorinated rubber composites was increased from approximately 200°C to 340°C[7].

Nitrile rubber (NBR), the copolymer of acrylonitrile and butadiene is used in many fields such as sealing element widely. It has good mechanical properties, moderate cost and excellent resistance to oils. CNTs/NBR composites were widely studied in recent years [8-10]. The research testified that multi-walled carbon nanotubes could improve the performance of nitrile and hydrogenated nitrile rubber nanocomposites prepared by melt compounding [8]. Yunlong Li et al proved that CNTs can enhance the tribology properties of nitrile polymer composites from an atomic point of view [9].

In this paper, the properties of CNTs/NBR composites were focused.

2. Experimental

2.1. Materials

The materials used for the preparation of CNTs/NBR composites are listed in table 1.
Table 1. The composition of CNTs/NBR composites

| Composition                                | Phr |
|--------------------------------------------|-----|
| Nitrile rubber (NBR)                       | 85  |
| Natural rubber (NR)                        | 15  |
| Carbon nano tubes (CNTs)                   | 0   |
| Stearic acid                               | 2   |
| Paraffin                                   | 1   |
| Antioxidant                                | 2   |
| Carbon black (CB)                          | 50  |
| CZ accelerator 1                           | 1   |
| Tetra methyl thiuram disulfide (TMTD)      | 1.5 |
| Zinc oxide (ZnO)                           | 5   |
| Aromatic oil                               | 4   |
| Sulphur                                    | 2   |

2.2. Mixture preparation
The carbon nanotubes were of (diameter<10 nm and length in the range of 1-2 mm) treated with nitric acid and then reacted with the silane coupling agent KH550. The carbon nanotubes with aminotized surface were got from that way, which had well function with nitrile rubber.

All the components were thrown into open rubber mixing machine at 50℃. Then the mixer was put on the vulcanizing press for 25min at 145℃ with the load of 20T. The resulting rubbers were kept at room temperature for 24 h before testing.

2.3. Mechanical properties
The rubber composites fleet were cutting into the standard size according GB/T 528-2009, samples for tensile were got from that. The mechanical properties were tested by electronic universal testing machine.

2.4. Thermal aging test
Some samples of tensile test were put into temperature and humidity regulator at 70℃ for 72h, then kept at room temperature for 24 h before testing.

2.5. Surface morphology
The morphology of the samples was sprayed by gold powder, and observed with a scanning electron microscope (SEM).

2.6. Akron abrasion test
Akron abrasion loss were got from akron abrasion test according GB/T1689-2014. The specimen with a width of 12.7mm and a thickness of 3.2mm was paste on the wheel with adiameter of 68mm at room temperature for 24h. The rubber wheel installed on the wheel shaft and was removed after 600 revolutions, then the surface was cleaned with a brush, and the rubber wheel was weigh by an electronic balance. The test started with a distance of 1.61KM (1341Rpm). The rubber wheel was clean and weight after the test.

2.7. Hardness
Shore durometer (AM) was used to test the hardness of rubber composites.

3. Results and discussion

3.1. Mechanical properties
Figure 1. The mechanical properties of CNTs/NBR composites in room temperature (a) and 70℃, 72h(b)

It can be seen from figure 1(a), the strength of rubber composites have tiny change with the increase of the content of carbon nanotubes. It may be due to that the carbon nanotubes have long length and diameter relatively, and which is difficult for them to follow the stretching orientation in rubber matrix. The CNTs are brittleness due to the larger rigidity while in strength action, so it has small reinforcing effect on rubber composites. At the same time, the elongation at break decreases with the increase of adding amount due to the high rigidity of carbon nanotubes.

It can be seen from figure 1(b), the tensile strength and elongation at break of rubber composites show a downward trend after aging, and the elongation decrease obviously. The variation range of tensile strength and elongation after break decreased gradually with the increase of the content of carbon nanotubes at the same time, which indicated that the addition of carbon nanotubes can improve the aging resistance of rubber composites and maintain the bulk performance of rubber composites. Which may probably due to that the carbon nanotubes are distributred in the rubber uniformly, which hinders the damage of free radicals to the double bonds in the rubber, thus reducing the aging process of the rubber.

3.2. Morphology
Figure 2. The microstructure of rubber composites with different content of CNTs, (a)0 phr (b)1phr (c)2phr (d)4phr (e)6phr

As can be seen from figure 2, after the matrix is frozen and brittle, some part of the carbon nanotubes is exposed on the surface of the matrix after brittle in liquid nitrogen. It can be seen that the carbon nanotubes are distributed in the matrix evenly. CNTs dispersed in the matrix and have an aggregation area. The dispersion of CNTs is well distributed when the content is 2phr and meanwhile the agglomeration phenomenon occurs when the content is 4phr.

3.3. Akron wear performance and shore hardness

It can be seen from table 2, the hardness and wear resistance of the rubber and the rigidity of the rubber system increased with the addition of CNTs. The elastic network structure formed by carbon nanotubes limits the movement of the rubber macromolecular chains due to the relatively slow wear process of akron and small material deformation, then the wear resistance of rubber was improving.

| The content of CNTs(phr) | 0   | 1   | 2   | 4   | 6   |
|--------------------------|-----|-----|-----|-----|-----|
| Abrasion loss(g)         | 0.336 | 0.323 | 0.318 | 0.312 | 0.305 |
| Hardness(H<sub>AM</sub>)  | 51.5 | 53.5 | 54.0 | 62.5 | 66.5 |

The surface morphology of the sample after akron abrasion test is shown in figure 3. A series of ridges parallel to the rotation direction of the sample appear on the rubber surface in the microscopic state. The abrasion pattern become dense and the surface have a significant change after the addition of CNTs, which reduce the wear loss effectively by adhesive wear and improve the wear resistance.
Figure 3. Morphology of the sample after akron abrasion test, (a) 0 phr (b) 1phr (c) 2phr (d) 4phr (e) 6phr

4. Conclusion
The strength of CNTs/NBR composites have tiny change with the increase of the content of carbon nanotubes, but the addition of carbon nanotubes can improve the aging resistance of rubber composites. The dispersion of CNTs is well when the content is 2phr, meanwhile the agglomeration phenomenon occurs when the content reaches 4phr. The wear resistance of rubber was improving due to the addition of CNTs.

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