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Study on the effect of carbon black, carbon nanotube on the properties of rubber blend acrylonitrile butadiene rubber (NBR)/polyvinyl chloride (PVC)

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Abstract

The effects of carbon nanotube (CNT) in combination with carbon black (CB) on the properties of acrylonitrile butadiene rubber (NBR)/polyvinyl chloride (PVC) (70/30) were investigated. The results reveal that the maximal tensile strength of the rubber blend was obtained by the fillers ratio of CB:CNT = 39:1. At this filler ratio, the thermal stability and heat conductivity of the rubber blend were also significantly improved. The analysis of FE-SEM images and DMA diagram indicate that the dispersion of filler as well as the interaction between fillers and rubber matrix was improved by the incorporation of CNT.

Keywords. NBR/PVC blends, carbon nanotube (CNT), carbon black (CB), nanocomposites.

1. INTRODUCTION

One of the most interesting polymer blends in materials science is the rubber blend of acrylonitrile butadiene rubber (NBR) with polyvinyl chloride (PVC) [1]. The elastomeric component NBR can act as a permanent plasticizer for PVC applications, as in electrical wires and cables coatings, wrapping films for the food industry, conveyor belts, domestic appliances, etc. The presence of PVC helps improve the ozone and aging resistance of NBR, which enable the use of this blend in the automotive industry as gaskets, wires and cables, and in the manufacture of soles, footwear, artificial leather and others [2, 3]. To increase the applicability of rubber materials as well as rubber blends, these materials are usually reinforced with a number of reinforcing fillers such as carbon black, silica, clay, etc. [4, 5]. The reinforcement capability of the fillers depends on their particle size, shape, dispersion and interaction with the polymer.

Carbon nanotubes (CNT) are one of the most popular nanoparticles which many researchers around the world are interested. CNT have great

potential to be used as reinforcement in composites because of their unique properties such as high mechanical strength and high electrical as well as thermal conductivity [6-9]. CNT's reinforcement is better than common fillers (carbon black, silica, clay, etc.). However, CNT are difficult to disperse and very expensive. The rubber nanocomposites that use only CNT as single filler is actually not relevant for certain industrial purpose. This is where the idea of combination CNT, graphene with carbon black seems more practical [10, 11]. H. Ismail et al. studied CNT combination with carbon black (CB) for natural rubber. The results showed that the curing time of the materials decreased as the CNT content increased. The tensile strength, elongation at breaks and fatigue life of the material were greatest with CB/CNT ratio of 29.5/0.5. At this ratio, the dispersion and interaction between CB, CNT with the natural rubber matrix are the best [10].

In this study, the combination of CNT with CB will create a resonant effect to enhance the mechanical and thermal properties of the NBR/PVC blend.

2. EXPERIMENTAL

2.1. Materials

- NBR/PVC blend is type NBR7030 (LG Chem. LTD., Korea).

- Carbon Nanotube (CNT) was supplied by Institute of Materials Science (Vietnam). The average diameter of CNT is between 60-80 nm, with a purity of 90 %.

- Carbon black is kind N330 (China).

- Additives: Sulfur, Sae-Kwang Chemical IND. No. Ltd. (Korea); zinc oxide, Zincolied (India); stearic acid, PT. Orindo Fine Chemical (Indonesia); DM and CZ accelerator; antioxidant D (China).

- Industrial ethanol 96° (Vietnam).

The basic ingredients in the rubber are shown in table 1.

Table 1: Formulations of the compounds

| No | Ingredients | Content (phr) |
|----|-----------------------|---------------|
| 1 | NBR/PVC (70/30) | 100 |
| 2 | Zinc oxide | 5.0 |
| 3 | Stearic acid | 1.0 |
| 4 | Antioxidant A | 1.0 |
| 5 | CZ accelerator | 1.5 |
| 6 | DM accelerator | 0.5 |
| 7 | Sulfur | 2.0 |
| 8 | Carbon black (CB) | 10÷50 |
| 9 | Carbon nanotube (CNT) | 0.5÷3.0 |

2.2. Preparation and characterization methods

- Preparation of rubber blends nanocomposite

+ First, disperse CNT in ethanol 96° with stirring and ultrasonic vibration, then the solvent to evaporate in part to gain CNT in paste form.

+ Then mixing CNT paste with NBR/PVC blend on the internal mixer (Brabender) at 100 °C, the speed of 50 rpm for 8 minutes.

+ After that, mixing NBR/PVC/CNT with carbon black and other additives on a two-roll mill at room temperature.

+ Finally, sheets of rubber blends were prepared for curing presses. The rubber blends was vulcanized at a pressure of 20 kG/cm², temperature of 155 °C, in 20 minutes

- Material Characteristics

Tensile properties are determined according to Vietnam Standard TCVN 4509-2006. The morphological structure was studied using Hitachi's S-4800 field emission scanning electron microscope (FESEM). Thermal stability was determined by

Thermogravimetric Analysis (TGA) on Setaram Labsys Evo S60/58988 (France) at a heating rate of 10°C/min in air. Dynamic Mechanical Analysis is carried out on a DMA 8000 from Perkin Elmer (Germany) with a constant frequency of 1 Hz, a heating rate of 3 °C/min from -100 °C to 100 °C in nitrogen. The thermal conductivity of the material was determined according to DIN EN 993-15 on Linseis THB500 instrument (Germany) with a power heater of 60 mW; measuring current: 20 mA; measurement time: 180 seconds. The sample size is 60x40x3 mm.

3. RESULTS AND DISCUSSION

3.1. The effect of carbon black on the mechanical properties

In this study, the technological factors as well as other additive components (accelerators, sulfur, stearic acid, ...) are fixed, only varying content of carbon black (CB). The results of investigating the effect of CB content on the mechanical properties of NBR/PVC (70/30) blend are shown in the following figures.

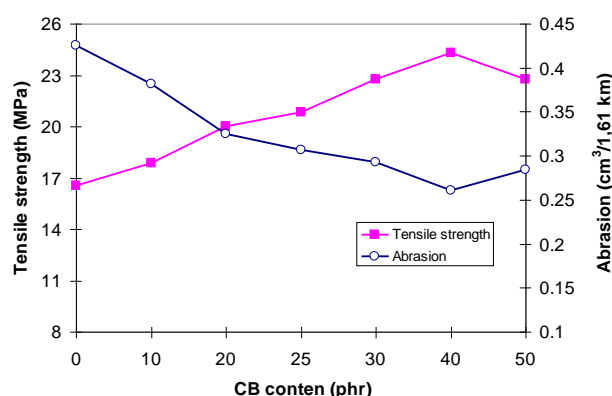


Figure 1: Effect of CB content on tensile strength and abrasion

The results in figure 1 show that, as the carbon black (CB) content increased, the tensile strength increased and the abrasion decreased. At 40 phr CB content, the tensile strength reached the maximum value and the abrasion reached the minimum value. If the CB content is greater than 40 phr, the tensile strength decreased and the abrasion increased. The variation in these values was due to the fact that the CB content is within the optimal range of CB particles forming their own network and splits the polymer macromolecules in all directions to form a hydrocarbon network. These two networks intertwine, forming a filler-rubber structure continuous that increases the mechanical properties of the material. As the CB content exceeds the

optimal content (greater than 40 phr) some CB particles do not join the CB network and it will form a separate phase. Thus, a fine dispersion of CB in rubber matrix is not obtained [4].

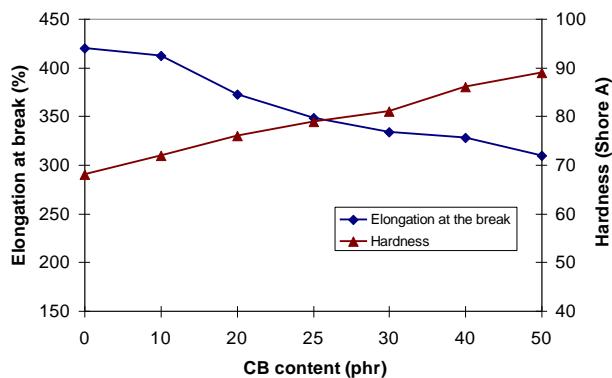


Figure 2: Effect of CB content on elongation at break and hardness

Meanwhile, the elongation at the break gradually decreased and the stiffness increased as the CB content increased. This can be explained, as the

increase in CB content will make the rubber molecules less flexible, hampering the bonding between them leading to reduced elongation at break and increased hardness of the material.

From the above results, CB content of 40 phr was chosen for further study.

3.2. Effect of CNT combination with CB on the mechanical properties

CNT possess high tensile strength of about 150 GPa, high elastic modulus of about 1200 GPa and high specific surface area that 500 times greater than that of carbon fiber. Therefore, this material has been considered as a research material used as a reinforcement material for polymers and only a small amount in the polymer, can improve the mechanical properties of materials. Carbon nanotubes also have the same chemical constituents as carbon atoms, so when combined with carbon black, they can have a resonant effect. Therefore, in this study, CB substitution by CNT was investigated into the mechanical properties of the material. The results are shown in table 2.

Table 2: Effect of CNTs content combination with CB on the mechanical properties of materials

| Samples | Tensile strength (MPa) | Elongation at break (%) | Hardness (Shore A) | Abrasion (cm ³ /1.61km) |
|-----------------------|------------------------|-------------------------|--------------------|------------------------------------|
| NBR/PVC/40CB | 24.28 | 328 | 86.0 | 0.261 |
| NBR/PVC/39.5CB/0.5CNT | 25.19 | 342 | 86.3 | 0.243 |
| NBR/PVC/39.0CB/1.0CNT | 27.01 | 353 | 87.0 | 0.226 |
| NBR/PVC/38.5CB/1.5CNT | 25.33 | 338 | 87.4 | 0.229 |
| NBR/PVC/38.0CB/2.0CNT | 24.54 | 323 | 88.0 | 0.236 |
| NBR/PVC/37.0CB/3.0CNT | 23.85 | 317 | 89.2 | 0.241 |

The results in table 2 showed that the tensile strength, elongation at break and abrasion resistance of the material reached a maximum value at 1 phr CNT. As the CNT content continued to increase (greater than 1 phr), these properties tend to decrease. This can be explained, as the CNT content exceeds the optimum value, CNT tend to bind to each other and reduce their ability to interact with the polymers matrix, leading to defects in the structure. The material structure leads to a reduction in the material properties of the material.

The hardness of the material increased because the CNT have a higher hardness than the CB. From these results, the CNT content to replace CB was 1 phr was selected for further study.

3.3. The morphological structure of the material

The morphological structure of NBR/PVC blends with CB and CNT was determined by FESEM. FESEM images of broken surfaces of typical material samples are shown in figure 3.

Results FESEM image shows that in NBR/PVC sample containing 25 phr CB, CB particles were relatively well dispersed in the rubber matrix. However, on the fracture surface of the material there is still agglomeration of CB particles. When the CB content increases to 40 phr, CB particles were still uniformly distributed in the rubber matrix. Therefore, the mechanical properties of the material reach the maximum value. When the CB content

continues to rise (50 phr), there is more agglomeration of CB particles that causes the material defects leading to decrease the mechanical properties of the material.

When replacing 1 phr CB by CNT, on the fracture surface of the material, carbon black particles disperse and interact better with rubber matrix. Therefore, with 1 phr CNT replacing CB has significantly improved the mechanical properties of the material.

3.4. Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis allows to determine the glass temperature (T_g) of polymers, storage modulus (E'), loss modulus (E''). The effect of temperature on the storage module of samples at 1 Hz is shown in figure 5. The E' value indicates the energy dissipation due to molecular motions, so E' represents the hardness of the material. The E' value depends on three factors: crosslinking density, dispersion filler content, dispersion particle size.

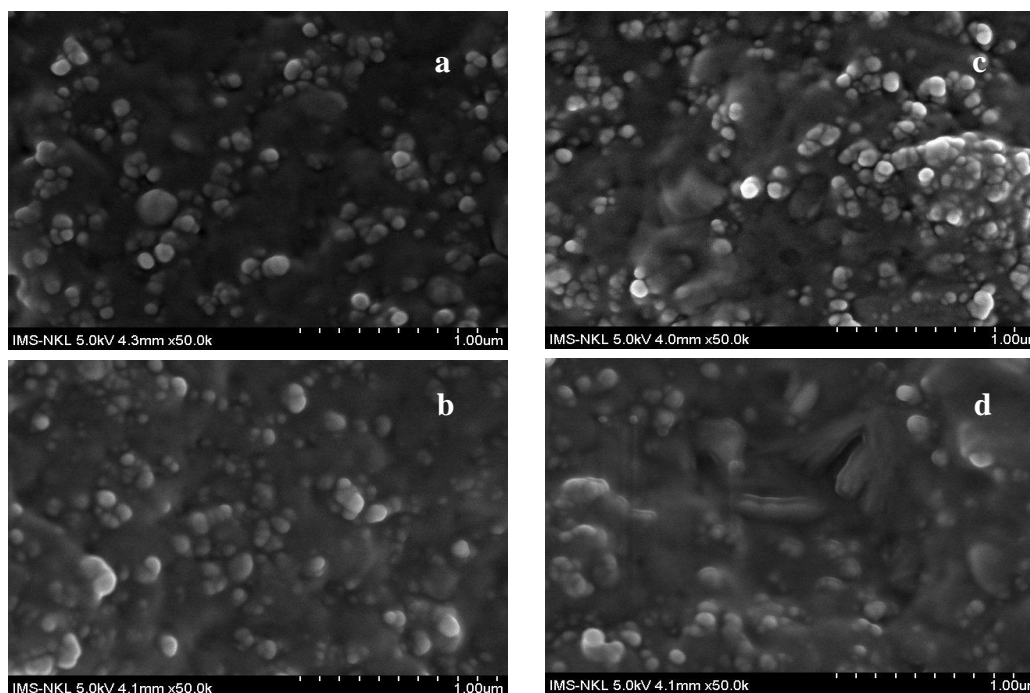


Figure 3: FE-SEM image of the fracture surface of the blend NBR/PVC with reinforcing fillers (a) 25CB; (b) 40CB; (c) 50CB and (d) 39CB/1CNT

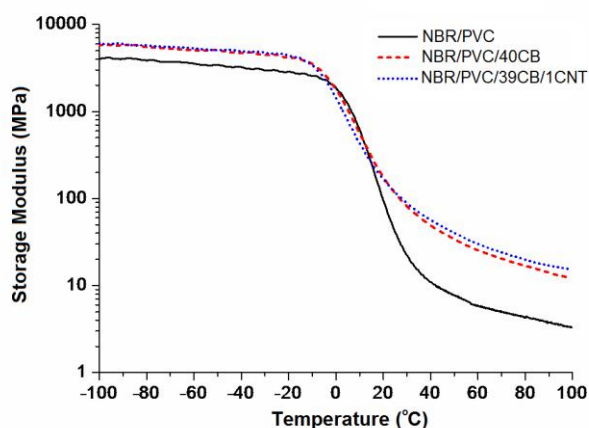


Figure 4: Storage modulus diagram of the samples based on blends NBR/PVC

The results in figure 4 show that the rubber blend samples have large storage modules at low temperatures, and then sharply decrease at the

transition area. For two rubber blends samples with reinforcing filler, the storage modulus of the material increased significantly, especially the sample containing 1 phr of CNT. This proves reinforcement of CNT in rubber blend, especially in the visco-elastic zone.

Results in figure 5 shows, NBR/PVC (70/30) rubber blend sample compatible well with each other (tan delta curve only appears a sharp peak with $T_g = 22.74$ °C). Two rubber blends samples with reinforcing filler, tan delta peak intensity and glass temperature decreases (due to storage module E' increases). In these two samples, rubber blend sample containing CNT has tan delta peak widths narrower. This demonstrates, when CNTs increased ability that scattered fillers dispersed more evenly, leading to increased interoperability between fillers with polymers matrix, similar to the report [11]. The Results in table 3 show that thermal stability of the

NBR/PVC blend is markedly improved with 40 phr CB through onset decomposition temperature increases (from 192.33 °C to 196.46 °C) and weight loss at 330 °C decreased (from 17.531 % to 13.412 %).

Therefore, the mechanical properties of the material are significantly improved.

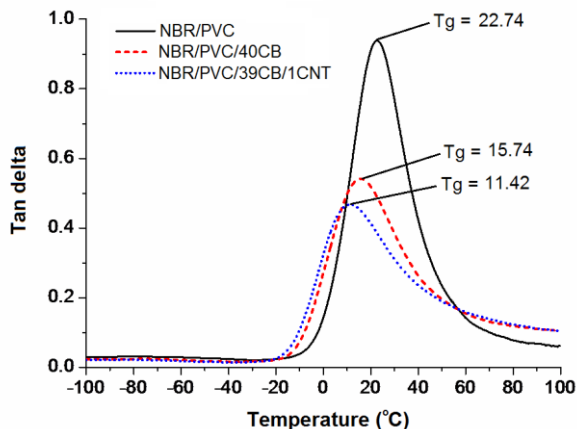


Figure 5: Tan delta diagram of the samples based on blends NBR/PVC

3.5. Thermal properties of the material

3.5.1. Thermal stability

The thermal stability of the material is evaluated by Thermogravimetric Analysis (TGA). The results of TGA analysis of material samples based on NBR/PVC blend are shown in figures 6-8 and table 3.

When replacing 1 phr CB by CNT, thermal stability of the rubber blend continues to rise (onset decomposition temperature increased by nearly 10°C). This can be explained, on one hand by the CNT heat resistance than CB, on the other hand due to the structure of the material is tighter (because CNT interacts well with the component polymers). Therefore, the thermal stability of the material is

significantly improved.

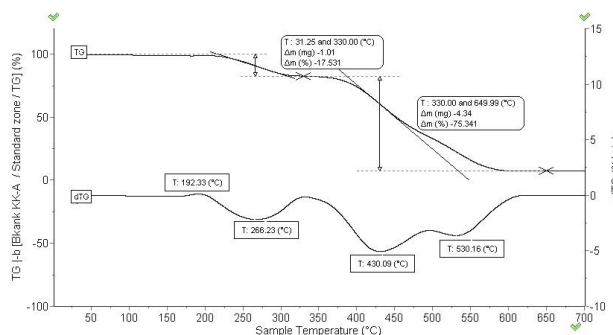


Figure 6: TGA diagram of NBR/PVC blend

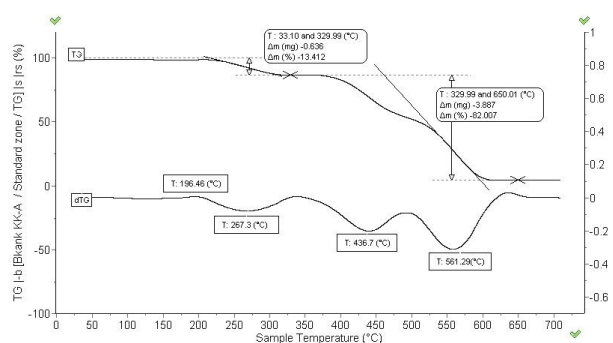


Figure 7: TGA diagram of NBR/PVC/40CB blend

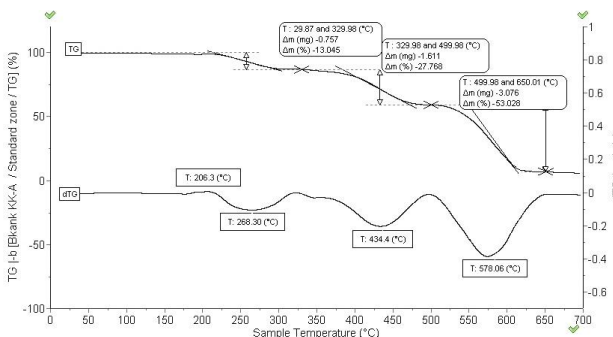


Figure 8: TGA diagram of NBR/PVC/39CB/1CNT blend

Table 3: Results of TGA analysis of the samples based on NBR/PVC blends

| Samples | T _{onset} (°C) | T _{max1} (°C) | T _{max2} (°C) | Weight loss at 330 °C (%) |
|-------------------|-------------------------|------------------------|------------------------|---------------------------|
| NBR/PVC | 192.33 | 266.33 | 430.09 | 17.531 |
| NBR/PVC/40CB | 196.46 | 267.30 | 436.70 | 13.412 |
| NBR/PVC/39CB/1CNT | 206.30 | 268.30 | 434.40 | 13.045 |

3.5.2. Thermal conductivity

To study the effect of CB and CNT on the thermal conductivity of the material, the samples thermal conductivity was determined on the Linseis THB 500.

The thermal conductivity of the samples on based NBR/PVC blend is shown in figure 9.

The results show that the thermal conductivity of NBR/PVC blend is unchanged with increasing temperature. In contrast, the thermal conductivity of

NBR/PVC filled with CB increased with increasing temperature. The effect of CNT on the thermal conductivity of NBR/PVC filled with CB and CNT was significant, especially at high temperature. By this sample, the thermal conductivity increases from 0.691 to 0.747 W/mK. The reason is due to the high thermal conductivity of CNT.

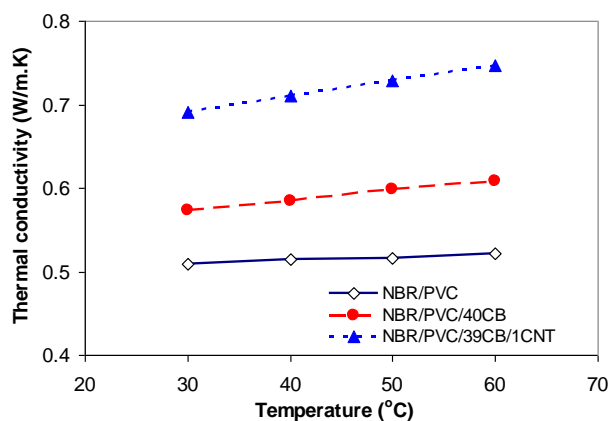


Figure 9: Thermal conductivity of NBR/PVC blends with temperatures

4. CONCLUSIONS

- The optimal CB content for NBR/PVC (70/30) blend is 40 phr. At this content, the tensile strength of the material increased by 47.1 % compared to the original sample. With greater contents of CB (50 phr), carbon black particles tend to agglomerate as tight structure of the material breaks down, leading to the mechanical properties of the material decreases.

- The appropriate CNT content to replace CB is 1 phr. With CB/CNTs ratio (39/1), the material is structurally tighter. The mechanical properties, thermal stability and heat conductivity of the NBR/PVC blend are significantly improved.

Rubber blend NBR/PVC/39CB/1CNT nanocomposite with high mechanical and technical properties can be used to manufacture technical rubber products, especially rubber products with abrasion resistance and high friction.

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