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Research Article

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Synergistic Effect of Silica with Carbon Nanotubes, Nanoclays and Whiskers on Physical and Mechanical Properties of Elastomeric Compounds Based on NBR

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ABSTRACT

The main objective of the present study was to investigate the synergistic effect of simultaneous use of two reinforcing fillers in rubber compounds based on NBR. Silica was used as reinforcing filler in all samples and the loading content was 25 phr. 3 phr of nanoclay, carbon nanotube and whiskers was used as second reinforcing filler in NBR/silica compounds. Melt mixing method was employed for compound preparation. The effects of nanoclay/silica, carbon nanotube/silica and whiskers/silica on mechanical and vulcanization characteristics of the rubber compounds were investigated. Vulcanization characteristics of compounds were determined by Monsanto Oscillating Disk Rheometer 100 at 150 ˚C. These results indicate that the presence of two reinforcing fillers greatly reduces the curing time and increasing the curing rate of compounds. A significant increase of the rubbery modulus was obtained upon filler addition. The reinforcing effect was particularly important for the compounds reinforced with 25 phr silica and 3 phr nanoclay and whiskers. However, this situation was not valid for carbon nanotube containing samples. Formation of nanoclay-silica, whiskers-silica and carbon nanotube-silica subassembly should be responsible for this synergism effect.

Key words: Silica, nanoclay, NBR, mechanical properties, synergistic effect

INTRODUCTION

Acrylonitrile-butadiene copolymer (NBR) is a special purpose elastomer and possesses attractive properties, such as good oil resistance, abrasion resistance, elastic properties and low gas permeability, and is widely applied in a wide range of industrial equipment [1]. However, the mechanical properties, ozone resistance and processibility of NBR are poor [2]. Fillers such as silica [3], carbon [4-7], layered silicates [5], and carbon nanotubes [1] are usually added to improve its mechanical strength [5]. The extent of property improvement depends on several factors including the size of the particles, their aspect ratio, their degree of dispersion and orientation in the matrix and the strength of interactions between the filler and the matrix polymer [1]. However, the addition of fillers has some limitations and desired properties cannot be achieved. The blending of NBR with other polymers, such as Polyurethane (PU), Polyvinyl Chloride (PVC), Styrene Acrylonitrile Copolymer (SAN) and Ethylene Propylene Diene Rubber (EPDM) can overcome these limitations.

In addition to above method, the idea of combination of fillers in order to make use of synergism effects which can be used as a convenient method to improve the properties of elastomeric compounds is discussed. In this regards, a combination of silica (SiO2) and carbon black (CB) in different matrix systems have been widely studied and have been concluded that the mixture of silica and CB has highly efficient to lower the rolling loss and to improve the wet skid resistance so as to produce green tires with limited energy consumption and CO2 emission from automobiles. Except carbon black, silica is one of the most important filler used in the NBR compound. Nitrile rubber exhibited the highest interaction with silica probably through the hydrogen bond between the –CN group and silanol groups. In addition, silica (SiO2) as reinforcing filler has been preferentially selected for preparing vulcanizates with a unique combination of tear strength, abrasion resistance, age resistance, and adhesion properties. To our best knowledge, there is no report on the use of combination of silica with other fillers such as nanoclay, carbon nanotube (CN) and whiskers (W) for improving the physical and mechanical properties of NBR compounds. In this regards, we investigated the synergistic effect of silica with carbon nanotube, nanoclay and whiskers on the physical and mechanical properties of NBR compounds.

DESIGN, MATERIAL, PROCEDURE, TECHNIQUE OR METHODS

Materials Used

The basic materials used in this work were: NBR with 45 wt% acrylonitrile (ACN) (Mooney viscosity, ML1+4, at 100 °C = 60) was provided by Polimeri Europa Co., Ltd. The precipitated silica (VN3) powder with a surface area 175 m^2/g comes from Evonik Degussa, Germany. Organically modified Montmorillonite clay Cloisite15A, was supplied by Southern Clay Products Inc., USA. Multi-wall carbon nanotubes (CNTs) with 10–20 nm outer diameter were made in Cheap Tube Co., Ltd. Whiskers (Gypsum-$CaSO_4$) were prepared by Guangzho Greeneer Chemical Technology Co. LTD, China. It is a kind of white crystal material with a density of 2.96 g/cm^3, diameter ranging from 0.2 μm to 2 μm, and length in the range of 10−100 μm. Other compounding (DOP oil) and curing additives (ZnO, Stearic acid, Sulphur, CBS, TMTD), including antioxidant (IPPD-4010) are commercial grades.

Sample Preparation

The all samples were prepared by melt compounding on a two-roll mill with a friction ratio of 1:1.4 at 50 ˚C. Vulcanization characteristics of the samples were determined by Monsanto Oscillating Disk Rheometer 100 at 150 ˚C. After mixing, the rubber compounds were left for 12 h and then molded in the form of sheets in an electrically heated hydraulic press at their optimum cures obtained from rheometer at 150˚ C. The denoted codes and composition of the samples are described in Table 1.

Table -1 Formulation of NBR-Compounds

Ingredients *	S1	S2	S3	S4	S5	S6	S7	S8
NBR	100	100	100	100	100	100	100	100
Silica	0	25	0	0	0	25	25	25
Nanoclay	0	0	3	0	0	3	0	0
CNTs	0	0	0	3	0	0	3	0
Whiskers	0	0	0	0	3	0	0	3
DOP	15	15	15	15	15	15	15	15
IPPD	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
ZnO	5	5	5	5	5	5	5	5
ST.A.	1	1	1	1	1	1	1	1
TMTD	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
CBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

* Amount indicated here is in parts per hundred gram rubber (phr) basis.

Sample Characterization

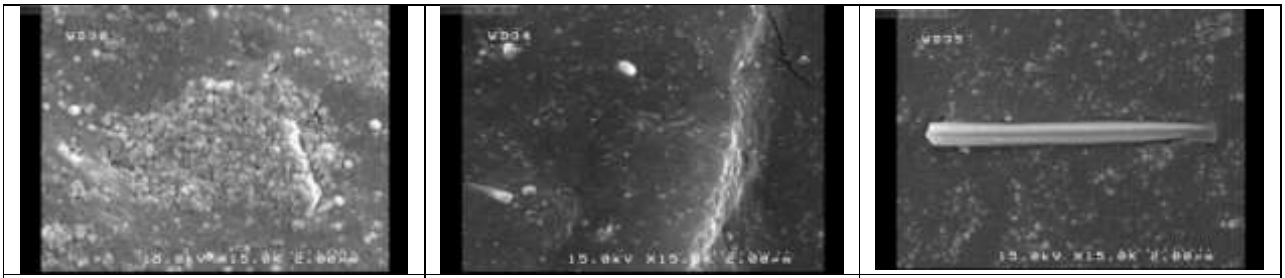
Scanning Electron Microscopy (SEM): The filler dispersion state was observed at different scales using scanning electron microscope, SEM, (Hitachi 4160, Japan) with 20 kV accelerating voltage. The cryogenically fractured surfaces were coated with gold for enhanced conductivity using SPI sputter coater.

Tensile properties: Tensile specimens were punched out from the molded sheets using ASTM Die-C. The tests were carried out as per the ASTM D 412 methods in a Gotech Testing Machines Inc. (Gotech/GT-7016-A, Taiwan) at a cross head speed of 500 mm/min. Results were averaged on five measurements. IRHD hardness was measured with a Zwick hardness tester according to the standard ASTM D2240. Oil aging condition was applied in a hot turbine oil at 120 °C for 24 hours at atmospheric pressure.

RESULTS AND DISCUSSION

Morphology

The states of the filler dispersions have been investigated with SEM. The SEM micrographs representative of each sample are reported in Fig. 1. As it can be seen all samples show good dispersion and distribution of nanoclay, CNT and Whiskers. It may be due to the good affinity between the reinforcing fillers with NBR matrix.



S6	S7	S8

Fig. 1 Scanning electron microscopy (SEM) observation of NBR compounds

Effect of Reinforcing Fillers on Vulcanization Characteristics

Vulcanization characteristics of the NBR compounds were summarized in Table 2.

Table -2 Vulcanization Characteristics of the NBR Compounds at 150 ˚C

	S1	S2	S6	S7	S8
MH (lb.in)	32	41.17	46.35	77.73	60.83
ML (lb.in)	5.53	5.49	7.27	17.54	13.22
MH-ML	26.47	35.68	39.08	60.19	47.61
t90 (min)	12	7	8	7	6

Minimum and maximum torques and the differences between them (MH-ML) for all NBR compounds are higher than that of for unfilled NBR. This increasing values was higher for CNT, nanoclay and Whiskers containing samples compare to the sample containing silica. This shows the reinforcing effect of this fillers in the NBR compounds and they have synergetic effect on the vulcanization characteristics of NBR compounds. Also, scorch and optimum cure times are longer when reinforcing fillers was used in the compound compared to the compounds without additives. The physical crooslinking between reinforcing fillers and NBR hindered the mobility of rubber chains. Lower deformation capability of NBR chains at certain torque, increase minimum requirement torque of rheometric vulcanization characterization. Hence, it can deduce that additives with high affinity with matrix chains and higher surface area have higher reinforcing effect on rubber and shows synergestic effect with different type fillers. MH-ML, is considered as the parameter to demonstrate the degree of chemical crosslinking. Chemical bonding of NBR chains with the functional groups on CNT, whiskers and nanoclay is occuring during vulcanization.

Mechanical Properties

Mechanical properties of the NBR compounds are shown in Table 3. All samples are exposed to oxidative aging at oil or ozone conditions. Failure can happen due to oxidative aging which results in loss of mechanical properties. Therefore, strong mechanical properties and aging stability are necessary in NBR compound design. Hardness values are found to be around 62 and that is higher than that of for NBR (53) and NBR comtaining silica as a filler (58).

Table -3 Mechanical Properties of the NBR Compounds

	S1	S2	S6	S7	S8
Hardness before Aging	53	58	62	60	62
Hardness after Hot Oil Aging	55	64	68	70	64
Maximum Stress before Aging (Mpa)	3.61	16.80	15.04	18.43	17.16
Maximum Stress after Hot Oil Aging (Mpa)	2.32	14.27	13.60	13.16	16.66

Hardness increases correspondingly with increasing the surface area of reinforcing fillers, as the number of rubber chains immobilized on the reinforcing fillers suraces grows up. This suggests that the external surface area of reinforcing fillers is indeed a major factor determining the hardness of NBR compounds. Oil aging has increased the hardness of unfilled NBR and NBR compounds. Reinforcing fillers increased the maximum stress of NBR compounds befor and after aging for all samples. It can be noticed that aging has decreased the modulus of neat NBR. Increasing the maximum stress of NBR compounds containing CNT, nanoclay and whiskers was higher that that of for NBR containing silica. It may be attributed due to the synergestic effects of silica with reinforcing fillers such nanoclay, CNT and whiskers.

CONCLUSION

The effects of nanoclay/silica, carbon nanotube/silica and whiskers/silica on mechanical and vulcanization characteristics of the rubber compounds were investigated. These results indicate that the presence of two reinforcing fillers greatly reduces the curing time and increasing the curing rate of compounds. A significant increase of the rubbery modulus was obtained upon filler addition. Formation of nanoclay-silica, whiskers-silica and carbon nanotube-silica subassembly should be responsible for this synergism effect.

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