Comparison of carbon nanotube and soot reinforced rubber mixtures and their mechanical-morphological properties

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Abstract— *In our study, we investigated 2 different natural rubber mixtures with CNT's and shoot. The aim was to compare the results of samples and their mechanical effects with a shore. A hardness tester, a tensile strength instrument before and after vulcanisation (t=30; 60; and 90minutes) during the UV-ageing processes. The hardness results represented the different after the degradation process that was 10 % different between the samples.*

***Keywords*— Rubber, CNT, UV light, degradation, soot, composites.**

I. INTRODUCTION

Elastomers have become a widely used technical material of our time. This is due, among other things, to the ability to produce significant reversible deformations of up to 100% by virtue of low tensions, and their mechanical and other properties can be altered in a universal spectrum by the correct selection of base materials and other ingredients. Their physical and mechanical properties can be greatly improved with – for example – fillers or reinforcing agents, and by adding the proper plasticizer they can be more or less easily used technologically. (e.g. acting as a slider). Although different additives play a key role regarding the properties of the finished rubber, the quantity and ratio of the additives cannot be freely altered since each component has a positive (soot as a filler improves abrasion resistance) effect, or greatly reduce certain properties (e.g. over-vulcanization with increased sulfur content):

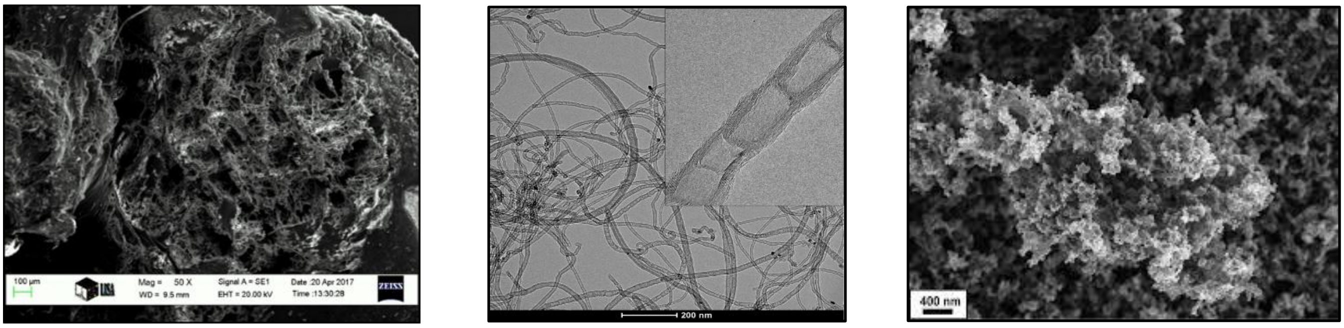

FIG. 1. SEM-Image of raw caoutchouc (50x magnification), CNT and Soot

Filler materials are isodynamic solid, matrix insoluble particle systems forming a separate solid phase. Their use has a remarkable past, and from the first quarter of the 19th century there are already references to the use of fillers in the caoutchouc. As a reinforcing filler, one of the largest quantities and the oldest used in the rubber industry are various soots. The most commonly used method for classifying them today is the 4-tag ASTM D1765 [1]. In the course of my investigations, we selected the 326 N type, in Table 1.

TABLE 1
PROPERTIES OF THE 326N TYPE SOOT ADDITIVE [1]

ASTM Classification	**OAN no., compaction** [10^{-5} m^3/kg]	**Coloring** [%]	**Density** [kg/m^3]	**Modulus** [MPa]
N326	68-69	110-113	446-470	-4,2 and -3,0

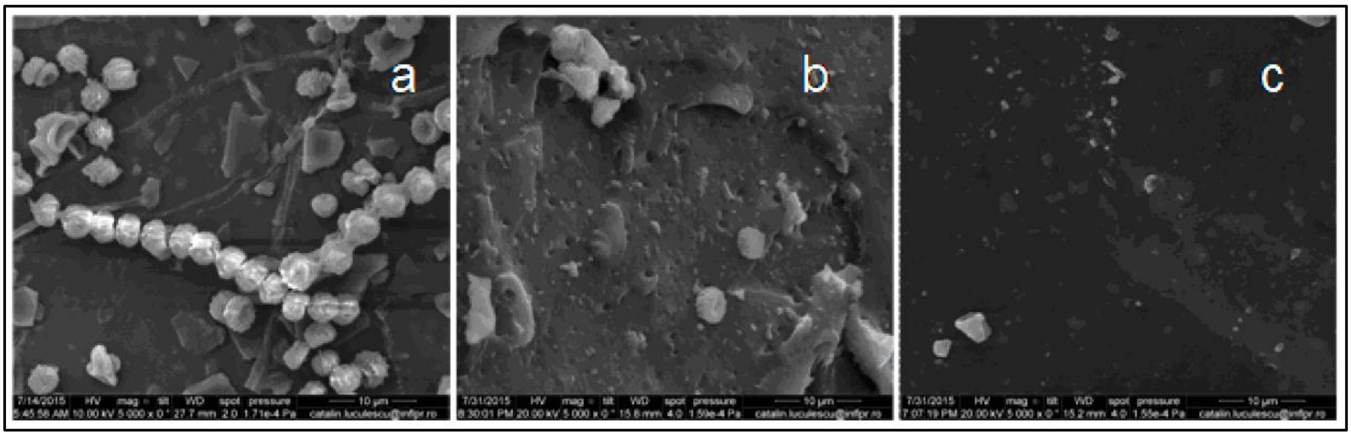

FIG. 2. SEM-image of NR-rubber mixtures cured with active fillers (10 µm) [2]

II. CARBON NANOTUBE-REINFORCE DRUBBER MIXTURES

Compared to the century-long history of carbon black, the intensive research of the possibilities of using modern nano reinforcements are limited to the last 1-2 decades. These fillers may be active or inactive, mineral, carbon based or biological, and are also distinguishable as plate, spherical and fibrous structures. Lopez-Manchado et al. [4] investigated nano composites produced by the NR matrix SWCNT reinforced laminated blending process, where it was found that SWCNT had a significant acceleration effect on vulcanization and also had a strengthening effect resulting from increased storage modulus and increased glass transition temperature of nano composites. These effects can be observed in most soot fillers, but on the basis of the results of the researchers, much more to SWCNT filling. Bokobza et al. [5] produced NR-MWCNT nano composites with toluene and then performed mechanical and conductivity tests, using unchanged mixtures as a basis.

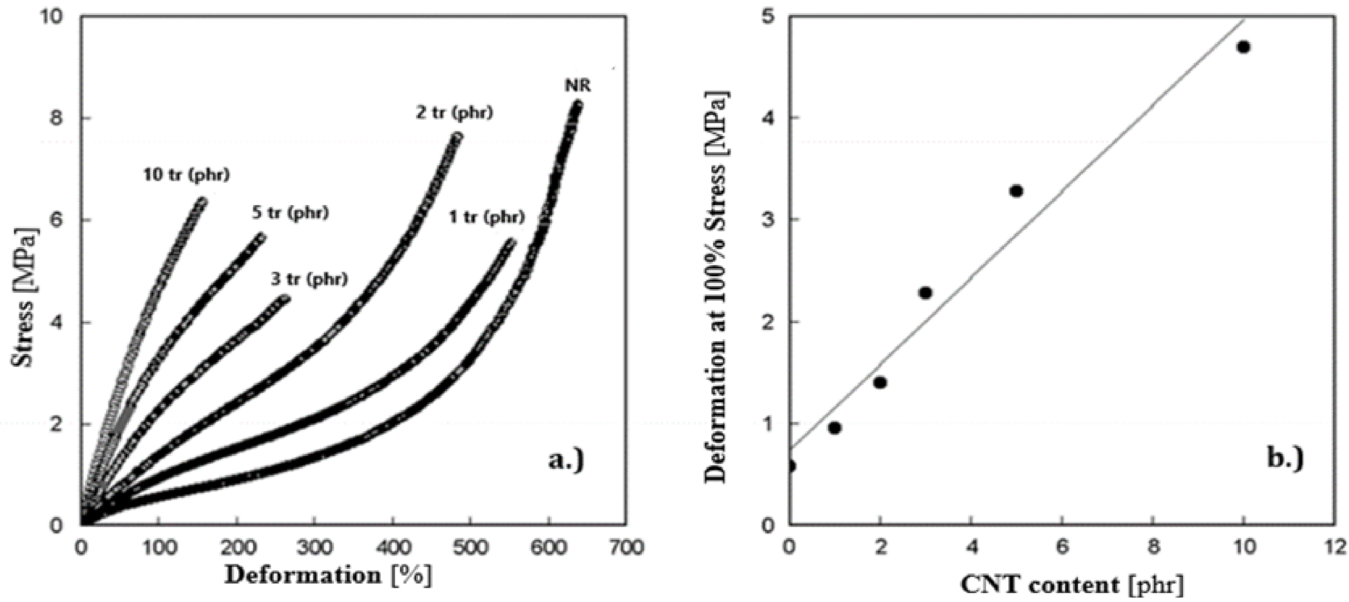

FIG. 3. Tension-deformation curves (a), and the tension-deformation curves of the NR-MWCNT composite according to carbon nanotube content (b) [2]

III. PRODUCTION RECAPTURES AND THE PRODUCTION OF SPECIMEN

Fillers, depending on their activity, alter the viscosity of the mixture, active soots and silica, increase viscosity. The first and definitive step of making the raw mix was the accurate measurement of the basic and additives at room temperature (T = 25°C ± 1°C) and normal relative humidity (50% ± 1%). The raw mixtures were homogenized in a cylinder at 35-40°C and the vulcanization process was carried out at T = 145°C, p = 220 bar and t = 10 minutes.

TABLE 2
OWN RECIPE BASED ON LITERATURE AND EMPIRICAL EXPERIENCES

Appliedmaterials	**Measuredquantities** [phr]	**Mixing Phases** [min.]
NR	100	60
Stearicacid	3	5
ZnO	5	5
ALTAX (MBTS)	0,6	5
Sulfur	2,5	5
Soot/CNT	50,7	20
NO	10	20

NO: Vegetable Oil ***120 min/batch***

IV. APPLIED TESTS

4.1 Mechanical testing: "Shore A" Hardnes test and Tensile strenght

Generally it can be stated that reinforcing fillers require substantially less per unit of hardness than half-active or inactive fillers. Soots enhance hardness more effectively than white fillers. Roughly speaking, fillers with smaller particle diameters and larger specific surface are more effective than fillers of larger diameter and smaller specific surface. The fillers effect on hardness is also dependant of the type of caoutchouc used. Caoutchouc with higher density requires smaller amounts of filler for a unit of hardness increase, than smaller density caoutchouc base materials. As described in the previous chapters, theoretically the oils, softeners, internal plasticizers reduce the hardness of the rubber which can be increased by adding more sulfur.

TABLE 3
TEST RESULTS BEFORE- AND AFTER THE AGING PROCESS

	Time	**0 min.**	**30 min.**	**60 min.**	**90 min.**
Soot	Average value	42,80	37,90	39,30	42,30
	Min. value	42,00	36,70	35,70	40,90
	Max. value	43,40	39,50	41,20	44,10
Nano	Average value	33,10	35,90	38,50	40,20
	Min. value	32,30	33,30	36,10	38,60
	Max. value	33,90	37,00	39,60	41,30

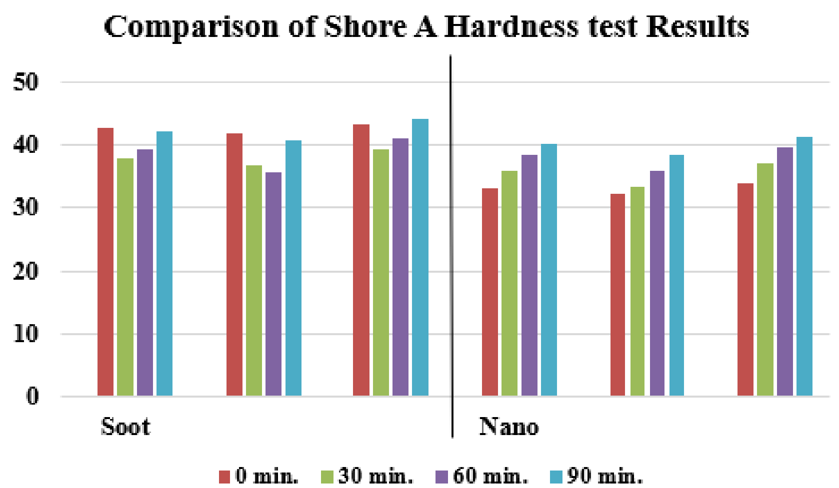

FIG. 4. COMPARISON OF INDIVIDUAL MIXTURES' SHORE A HARDNESS TESTS

4.2 Morphological and surface measurements: FT-IR spectroscopy and SEM microscopy

The next step in our investigations was surface-microscopic control of vulcanizates. Our goal was to observe the diffusion, possible migration of additives, and to follow up on aging processes. We have successfully determined that the efficiency of miscibility (mixing) has been successful; both filling systems are compatible with the raw rubber. We used a Bruker Tensor FT-IR for surface analysis and a Zeiss SEM-EDS for processes requiring higher resolution.

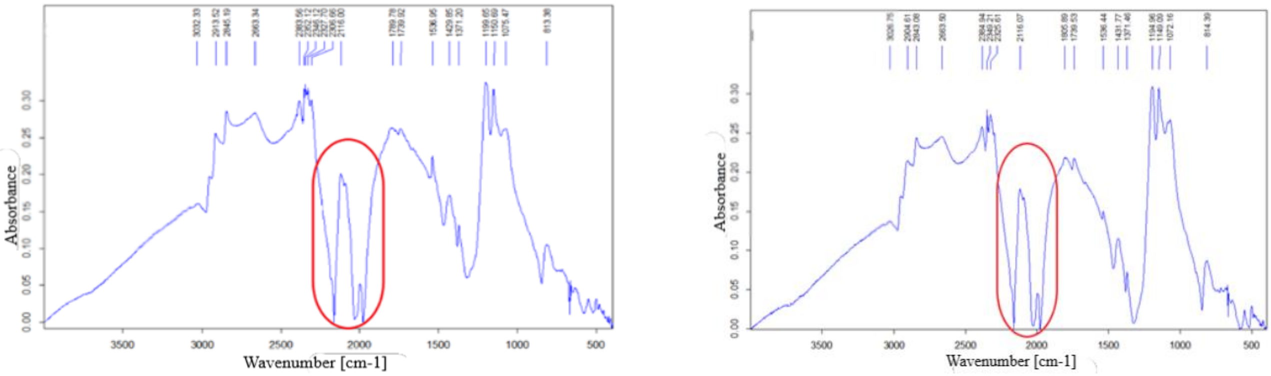

FIG. 5. Absorbance wave number of soot-cured,(a), nanotube-cured (b) vulcanised specimen before aging

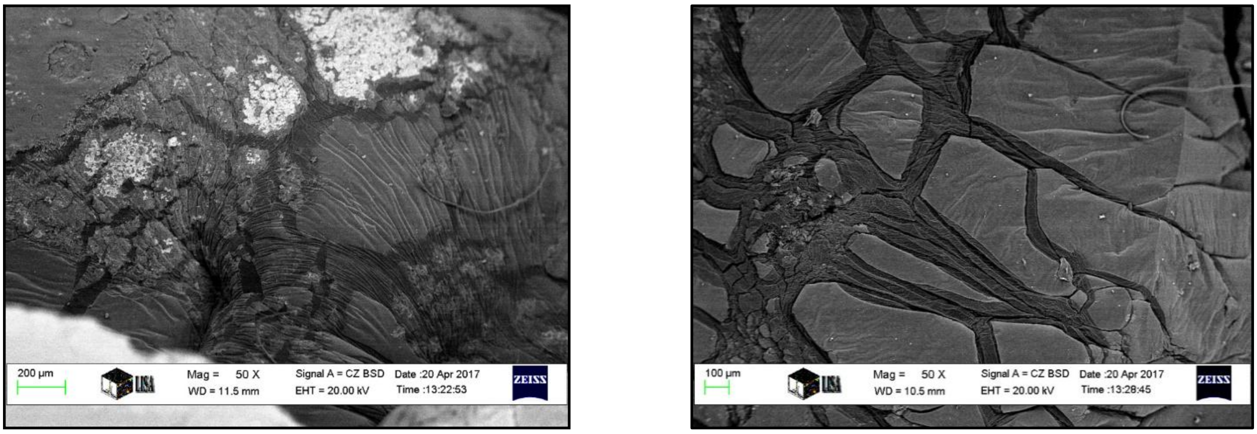

FIG. 6. SEM Images of soot-cured (a) and nanotube-cured (b) vulcanized specimen (50x magnification)

As shown on the figures above, the aging process had effect on both of the samples which appeared in the form of cracks on the surface, also gray-white areas are visible on the soot-treated specimen that may be caused by deta chingstearic acid. This is supported by SEM microscopic shots at 50x magnification, while the FT-IR device has only demonstrated the presence of fillers in the system, it cannot provide an adequate quantitative value, which is certain that a peak of similar intensity of 2000 cm^{-1} for both samples. This is the wavelength range and the vibration frequency of the carbon atoms in the carbon nanotube.

V. SUMMARY

The purpose of our research was to examine the mechanical and aging properties of two rubber mixtures, one of which was filled with a common industrial carbon, while the other was filled with a single-walled carbon nanotube.Mechanical testing was a Shore A hardness measurement series that was repeated before aging and after aging (0, 30, 60 and 90 minutes). The results supported our expectations that the surface degradation processes caused by UV light and ozone can be traced by changing the mechanical properties of rubber mixtures. In addition, surface morphological devices have been able to confirm the deterioration, which were present in the form of cracks on sample surfaces. At the same time, an unexpected problem occurred in the case of the soot cured mixture, in the presence of gray "blossoms" on the SEM images, which were suspected to have detected stearic acid stabilizer in the future more seriously. In the future, we would like to take a more serious look at this problem, since the compatibility of the stabilizer and the raw material, has impact on the initiation of the accelerated aging of the rubber, which can lead to high performance deterioration and reduced life expectancy.

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