

# Evaluation of mechanical and dynamic mechanical properties of multiwalled carbon nanotube-based ethylene–propylene copolymer composites mixed by masterbatch dilution

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## Abstract

A two-step masterbatch mixing technique was studied for preparation of carbon nanotube-filled ethylene–propylene diene elastomer compounds, and compared to conventional one-step mixing process. In the two-step process, a masterbatch compound with carbon nanotube content of 50 parts per hundred was prepared by melt-mixing ethylene–propylene diene elastomer. This material was then compounded with pristine ethylene–propylene diene elastomer and composites with different carbon nanotube concentrations were compared. The aim of this study is to compare the efficiency of two different mixing processes on the dispersion of carbon nanotubes and to facilitate the handling of carbon nanotubes, as the masterbatch can be prepared in a controlled way and used for further dilution without the problems related to carbon nanotube processing. The compound properties were studied with emphasis on mechanical characterization and dynamic mechanical thermal analysis. Masterbatch mixing resulted in the similar mechanical properties of the composites compared to the direct mixing method. At the relatively low loadings of carbon nanotubes, the considerable improvements of the mechanical properties were observed. The aspect ratio of the carbon nanotubes determined by transmission electron microscope was found to be similar to the one calculated from the Guth equation. It showed a considerable reduction in aspect ratio independent of the used mixing method.

## Keywords

Carbon nanotube, masterbatch mixing, rubber, EPDM

## Introduction

Carbon nanotubes (CNTs) have high potential for reinforcement due to their small dimensions, high aspect ratio, and unique properties arising from their tube-like structure. However, their application in a polymer, more specifically in rubbers, is hampered due to dispersion problems, as well as health and safety issues caused by the small particle size of the nanotubes. In many studies, solution mixing was used to improve dispersion, but this is a rather slow method and industrially not viable. Thus, for large-scale use, traditional mixing method where rubber compound is prepared by solid state and dry mixing of fillers, rubbers and all other additives in internal mixer or open two-roll mill is more practical method. The

masterbatch dilution technique is one of the methods whereby a fine dispersion and distribution of different nanosized fillers could be realized. This approach has been used previously for the preparation of nanoclay-based rubber nanocomposites.<sup>1</sup> In this work, a polar

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rubber, that is, carboxylated nitrile rubber (XNBR), was used as a matrix for the nanoclay masterbatch. This nanoclay-XNBR compound was then further diluted in a solution butadiene rubber matrix.<sup>1</sup> In another study, a similar type of XNBR-nanoclay masterbatch was exploited in the preparation of styrene butadiene/butadiene rubber (SBR/BR) nanocomposites.<sup>2</sup> In this study, it is reported that the final composites prepared in an internal mixer showed better mechanical properties compared with the composites prepared by a two-roll mixing mill or solution mixing.<sup>2</sup>

During rubber mixing process, a huge amount of fine chemicals and fillers are handled and due to this the working environment becomes poor: the chemicals can be found in the air and nearby areas. Therefore, the workers who are directly handling the CNTs in the mixing room can be affected by small nanoparticles by inhalation. There are reports about the toxicity of CNTs to the human health.<sup>3,4</sup> Precautions are needed to avoid possible penetration of CNTs into the human body by inhalation, by direct skin contact, by food and drinking water. These nanoparticles, when exposed to a considerable amount, can affect microorganisms, plants, and animals.<sup>3,4</sup>

To avoid these problems, the masterbatch dilution approach could be used. This technique allows preparing a masterbatch with a high CNT loading and further diluting it with the matrix material to the desired loading. Thus, it offers eco-friendlier and healthier compounding of rubber filled with CNTs.

Kummerlöwe et al.<sup>5</sup> prepared CNT masterbatches with two different types of rubbers, and finally it was diluted with SBR or nitrile rubber. It is reported that direct melt mixing of CNTs with S-SBR and NBR can establish a very low percolation threshold of 0.2 and 1 wt% CNTs, respectively.

In the present study, the application of the masterbatch technique for multi-walled CNT filled ethylene-propylene diene rubber (EPDM) and the effects of this mixing method on the resulting compound properties were studied. EPDM was selected as the elastomer matrix since it has good environmental resistance but relatively low mechanical properties which could thus be improved by the CNT addition. Furthermore, EPDM-CNT based materials have potential applications in electronics, for example, in flexible sensors.<sup>6,7</sup>

## Experimental

### Compounding and sample preparation

EPDM rubber (Keltan 512, Lanxess/DSM, the Netherlands) was used for the preparation of the masterbatch and the final compounds. Multiwall CNTs

**Table 1.** Calculated CNT content of the test compounds and TGA results.

Sample name	Mixing method	CNT content (phr)	CNT content (phr)
		Calculated	TGA result
EPDM_0	Masterbatch	0	0
EPDM_3	Masterbatch	3.2	3.3
EPDM_6	Masterbatch	6.3	6.3
EPDM_9	Masterbatch	9.3	8.7
Reference_6	Direct mixing	6.3	5.9

(NC7000) were purchased from Nanocyl, Belgium and used as received.

The masterbatch of EPDM and CNT was first prepared by mixing them 4 min in an internal mixer (Brabender N 350 E, rotor speed 70 r/min, starting temperature 50°C) with a composition of 2:1, that is, the CNT content of 50 parts per hundred (phr). A certain amount of this masterbatch was then further mixed in a separate step with pristine EPDM to CNT concentrations given in Table 1. After 2 min mixing 2 phr ZnO and 5 phr stearic acid were incorporated. The second mixing step was performed in the same mixer than the masterbatch with the similar mixing parameters. The compound was dumped at the temperature of 160°C or after 5 min mixing. Finally, 2 phr dibutyldithiocarbamate (ZDBC) and 1 phr N-cyclohexyl-2-benzothiazolesulfenamide (CBS) and 1 phr sulphur were added on a two-roll mixing mill. A reference sample was prepared by direct mixing of CNTs with EPDM for comparison (reference, 6 phr). Vulcanized samples with thickness of 2.2 mm were prepared by curing at 160°C during their respective curing time.

### Characterization

The curing behavior and the strain sweep analysis of the compounds were studied with the Advanced Polymer Analyzer (APA 2000, Alpha Technologies). Curing studies were performed at 160°C at 0.2° strain and 1.7 Hz frequency. The strain sweep was done with amplitudes from 0.28% to 140% at 100°C.

Thermogravimetric analysis (TGA) was done with a Perkin Elmer STA 6000. The measurements were conducted in air at a heating rate of 10 K/min from 30°C to 995°C.

Tensile properties were determined according to ISO 37 using a dumbbell specimen type 1. The tests were performed with a Messphysik Midi 10-20 universal tester, a contact extensometer and at a crosshead velocity of 500 mm/min. The Shore A hardness was recorded according to ASTM D 2240-00 with an AFFRI

Hardness tester, stand Type 1, at 15 s. Five parallel measurements were taken for tensile and hardness properties.

The thermomechanical behavior of the cured compounds was studied by dynamic mechanical thermal analysis (DMTA). The measurements were done on a Perkin Elmer Pyris Diamond DMTA and were performed in the range from  $-80^{\circ}\text{C}$  to  $+70^{\circ}\text{C}$  at a rate of 3 K/min and frequency of 1 Hz. They were started in force control in the glassy state and changed to displacement control after the initial reduction of the modulus due to the glass transition. The displacement limit was set to  $\Delta L = 40\ \mu\text{m}$  and with a sample length of 20 mm, the sample experienced 0.2% maximum strain during the measurement.

The tensile stress softening behavior (Mullins effect) was studied with a Zwick Z 010 according to DIN 53504/S2/200 with an optical extensometer. The prestress was 0.4 Newton, and the crosshead speed was 200 mm/min. The samples were first stretched up to 100% elongation and then released. This cycle was repeated three times after which the samples were stretched to failure. Transmission electron microscopic images were taken by a Libra 120 transmission microscope at an acceleration voltage of 120 kV. Samples were sliced by ultramicrotomy at the temperature of  $140^{\circ}\text{C}$ . The aspect ratios of CNTs for the analyzed samples were calculated from the well-dispersed areas of all high-resolution (original magnification 20,000 $\times$ ) images using ImageTool 3.00.

To study the aspect ratio analytically, Young's modulus values were fitted to two well-established mechanical models. The models were selected to have a single fitting parameter, the aspect ratio. The output of the models in each case is the filled compound (composite) modulus,  $E_c$ , as the function of the filler volume fraction,  $V_f$ .

When starting from the hydrodynamic effect caused by rod shaped fillers (Guth equation<sup>8</sup>) with aspect ratio of filler  $f$  in a matrix with modulus  $E_m$ , the modulus of the composite  $E_c$  can be calculated as

$$E_c = E_m \left( 1 + 0.67fV_f + 1.62f^2V_f^2 \right) \quad (1)$$

Composite models based on stress and strain distribution calculations were the second approach taken into account. The semi-empirical Halpin–Tsai model<sup>9</sup> for short-fiber reinforced composites was applied in the form of following equation

$$\frac{E_c}{E_m} = \frac{1 + 2f\eta V_f}{1 - \eta V_f} \quad (2)$$

where  $f$  is the aspect ratio,  $\eta = \frac{E_{filler}/E_m - 1}{E_{filler}/E_m + 2f}$  and  $E_{filler}$  is the Young's modulus of the filler. Equation (2) has

previously been used for CNT reinforced SBR, and following that approach, a CNT modulus value of  $E_{filler} = 1000\ \text{GPa}$  has been used.<sup>10</sup>

Beyond the modeling based on tensile testing data yielding the aspect ratio, also (DMTA) data was fitted for understanding the thermorheological behavior of the compounds. The approach used was based on finding the constants for the Havriliak–Negami equation (equation (3))<sup>11</sup>

$$E^*(\omega) = E_{\infty} + \frac{E_0 - E_{\infty}}{[1 + (i\omega\tau)^{\alpha}]^{\beta}} \quad (3)$$

where  $E^*$  is the complex modulus,  $\omega$  is the angular frequency, and  $\tau$  is the relaxation time,  $E_{\infty}$  and  $E_0$  the high and low frequency limits, correspondingly, and  $\alpha$  and  $\beta$  curve shape parameters.

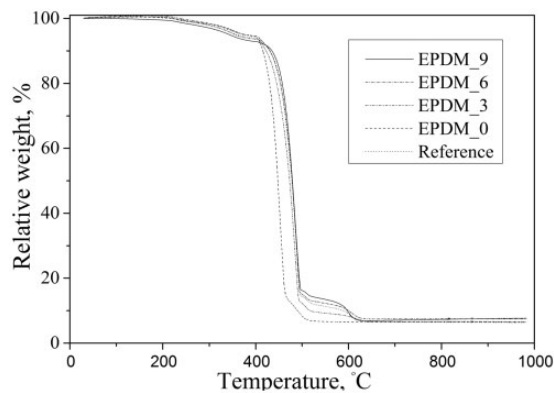
This method has previously been applied to study the  $\alpha$ -transition ( $T_g$ ) of plasticized polyvinylchloride (PVC) and carbon black (CB) filled neoprene,<sup>12</sup> unfilled copolyester and its nanosilicate filled variant,<sup>13</sup> and polycarbonate and polyether ether ketone thermoplastics.<sup>14</sup> Besides the glass transition ( $\alpha$  transition), also secondary transitions below  $T_g$  of ethylene–norbornene copolymers<sup>15</sup> have been studied with this approach.

## Results and discussion

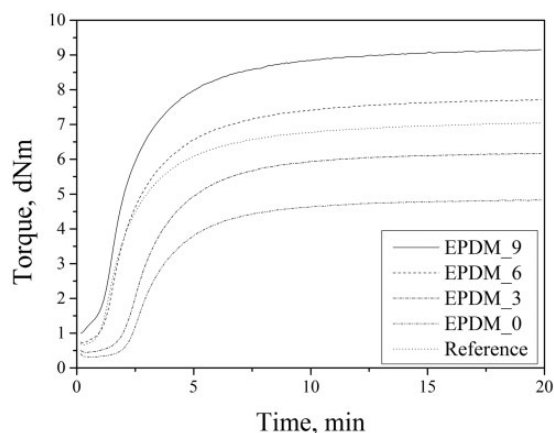
To determine the amount of CNTs which was effectively transferred into the rubber composites by masterbatch dilution process, TGA was done. The results obtained from this experiment are shown in Figure 1. Degradation of the composite took place in two steps: the first degradation step occurs in between  $400^{\circ}\text{C}$  and  $550^{\circ}\text{C}$  which is associated with the degradation of the polymer chains, and the second step takes place between  $550^{\circ}\text{C}$  and  $650^{\circ}\text{C}$ . This second degradation process can be ascribed to the oxidative decomposition of CNTs. The residue which is left in the pan is the amount of inorganic ingredients used in the compounding recipe. Based on the TGA data, the experimentally obtained CNT contents correspond well to the amount which was considered in the mixing process as seen in Table 1.

The most interesting observation of the TGA study was the overall increase in the degradation temperature of the rubber polymer. The thermal stability of the composites was found to improve nearly  $10^{\circ}\text{C}$  compared with the gum compound. This effect is found for all CNT-filled composites indicating good rubber-filler interaction.

To understand the effect of the addition of CNTs on the curing behavior, rheometric studies were performed (Figure 2). The curing parameters obtained from the



**Figure 1.** Thermal decomposition of the CNT-filled EPDM compounds.



**Figure 2.** The effect of the CNT concentration and the mixing method on curing behavior of EPDM.

curves are presented in Table 2. The cure rate index (CRI) which is a measure of the fastness of the cure can be calculated with the equation

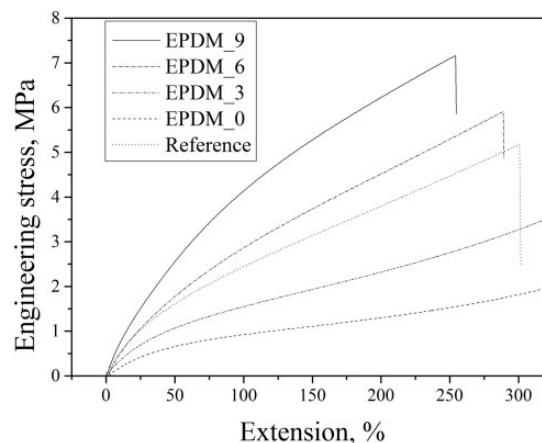
$$CRI = \frac{100}{t_{90} - t_2} \quad (3)$$

where  $t_{90}$  is the optimum curing time and  $t_2$  is the scorch time.

As can be seen in Figure 2, the increase in the rheometric torque of pure EPDM rubber is lower compared with filled compounds. With the increasing CNT concentrations, the torque values are increasing. Generally, presence of reinforcing fillers in soft rubber compounds enhances the rheometric torque which is explained by strong rubber–filler interactions. Besides the hydrodynamic effect of the filler particles, the formation of filler–filler network also contributes to higher torque values, and the effect can be observed from the minimum rheometric torque level.

**Table 2.** Curing data.

Name	$t_2$ , min	$t_{90}$ , min	CRI, 1/min	Delta torque, dNm
EPDM_0	1.6	7.6	16.7	4.5
EPDM_3	1.3	7.2	16.9	5.6
EPDM_6	0.7	6.7	16.7	7.0
EPDM_9	0.4	6.2	17.2	8.2
Reference	0.7	6.4	17.5	6.4



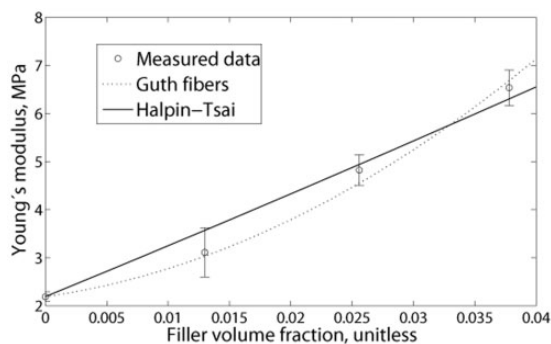
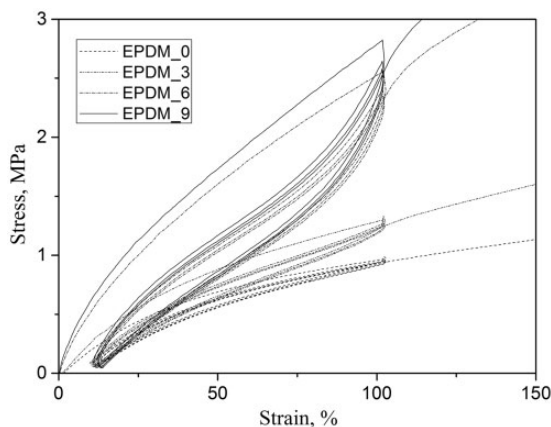
**Figure 3.** The effect of the CNT concentration and the mixing method on stress–strain behavior of EPDM.

The CRI (Table 2, column 4) increases at higher CNT concentrations. This indicates that the CNTs accelerate curing. In addition, the scorch time shortening with increasing CNT loading is notable; it is possible that this is due to remaining metal catalysts (e.g., Fe, Co, Ni)<sup>16</sup> from CNT production interfering with the onset of the curing reaction.<sup>5</sup> The reference compound shows higher CRI values than the corresponding masterbatch compound. Thus, the mixing method has some influence on the curing kinetics. As previously discussed by Kummerlöwe et al.<sup>5</sup> for CNT-filled NBR and SBR, competing mechanisms affect the cure process when CNTs are added, and the influencing factors include increased thermal conductivity, adsorption of accelerators and polymers on the CNT surface, and also the residual metal contaminants and CNT surface functionalities,<sup>5</sup> making it difficult to separate the effects.

Typical stress–strain curves of the masterbatch compounds and the reference are shown in Figure 3. The tensile properties derived from these curves are given in Table 3. The Young's modulus was calculated from the stress–strain curve within the linear range used for the slope determination (2–12% elongation for all materials).

**Table 3.** The mechanical properties of the CNT-filled EPDM composites.

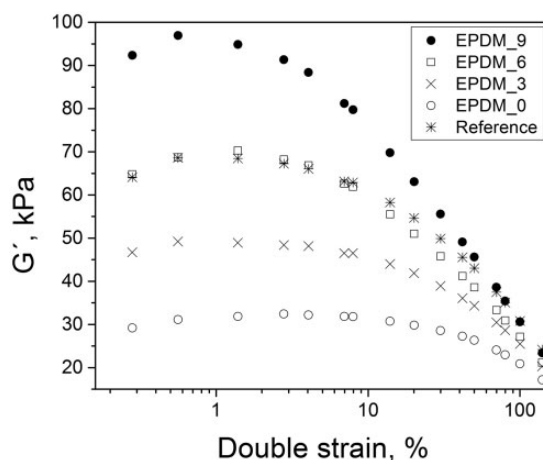
Sample	Tensile strength (MPa)	Elongation at break (%)	100% modulus (MPa)	Young's modulus (MPa)	Hardness (Shore A)
EPDM_0	2.1 ± 0.1	280 ± 30	1.0 ± 0.1	2.2 ± 0.1	42 ± 2
EPDM_3	3.5 ± 0.1	300 ± 20	1.6 ± 0.1	3.1 ± 0.5	49 ± 1
EPDM_6	5.5 ± 0.2	290 ± 20	2.7 ± 0.1	4.8 ± 0.3	53 ± 2
EPDM_9	7.0 ± 0.3	270 ± 10	3.9 ± 0.3	6.5 ± 0.4	57 ± 1
Reference	5.1 ± 0.2	290 ± 10	2.4 ± 0.1	4.5 ± 0.1	54 ± 1

**Figure 4.** Young's modulus values of CNT-filled EPDM fitted with Guth and Halpin–Tsai equations.**Figure 5.** Cyclic stress–strain curves of the CNT-filled EPDM rubbers.

It is clear from the Table 3 that with the increasing content of CNTs the tensile strength of the composites increases whereas the elongation at break values do not alter much. As expected, the stress at 100% strain increased monotonically with the increase in the filler content. A 4-fold increase in the 100% modulus can be observed when the EPDM was filled with 9 phr of CNTs. Similarly, the Young's modulus increased steadily with increasing filler content. As far as the tensile properties of directly mixed compounds (reference) are

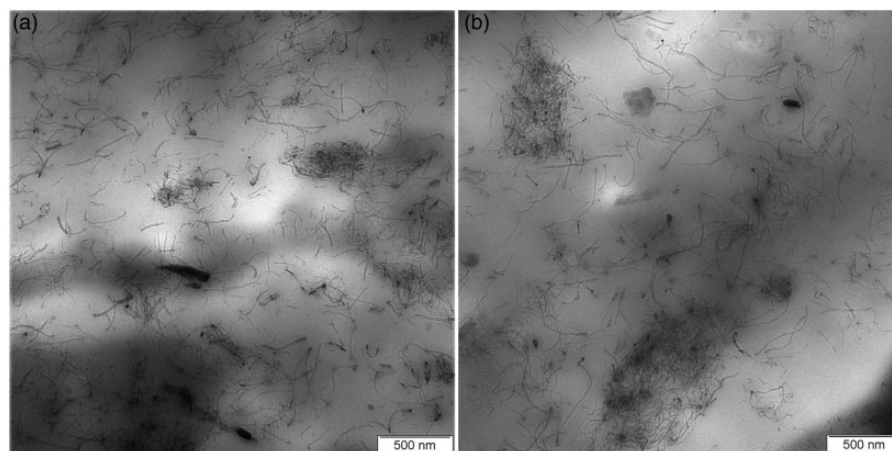
**Table 4.** Hysteresis areas, arbitrary units.

Sample	1st/2nd	2nd/3rd	3rd/4th
EPDM_0	5.6	0.8	1.1
EPDM_3	11.2	1.6	1.14
EPDM_6	46.0	3.9	2.01
EPDM_9	51.6	5.0	1.60

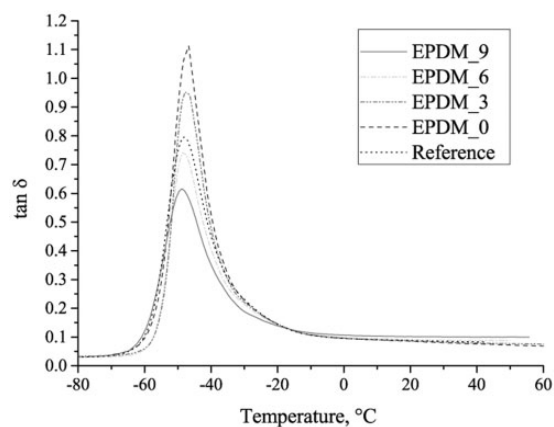
**Figure 6.** Storage moduli of the EPDM compounds as a function of dynamic strain (strain sweep analysis).

compared with EPDM\_6, significant variation could not be observed as the tensile strength values and other properties remain almost unaltered. This observation leads to the conclusion that the reinforcing effect of CNTs is not affected by the two-step mixing process. Particularly, a longer mixing time could break or damage the CNTs resulting in shorter tubes with a lower aspect ratio. Though the total mixing time of masterbatch procedure is longer than of the direct mixing process, the tubes apparently did not suffer much from the extra high shear mixing period. Shore A hardness values are not influenced by the way of mixing as seen in Table 3. Again it indicates that the





**Figure 7.** TEM images of the samples prepared by different mixing processes. (a) EPDM\_6, masterbatch-mixing, (b) directly mixed reference.



**Figure 8.** Loss angle ( $\tan \delta$ ) of EPDM compounds as a function of temperature.

masterbatch dilution process did not affect the reinforcing capabilities of CNTs.

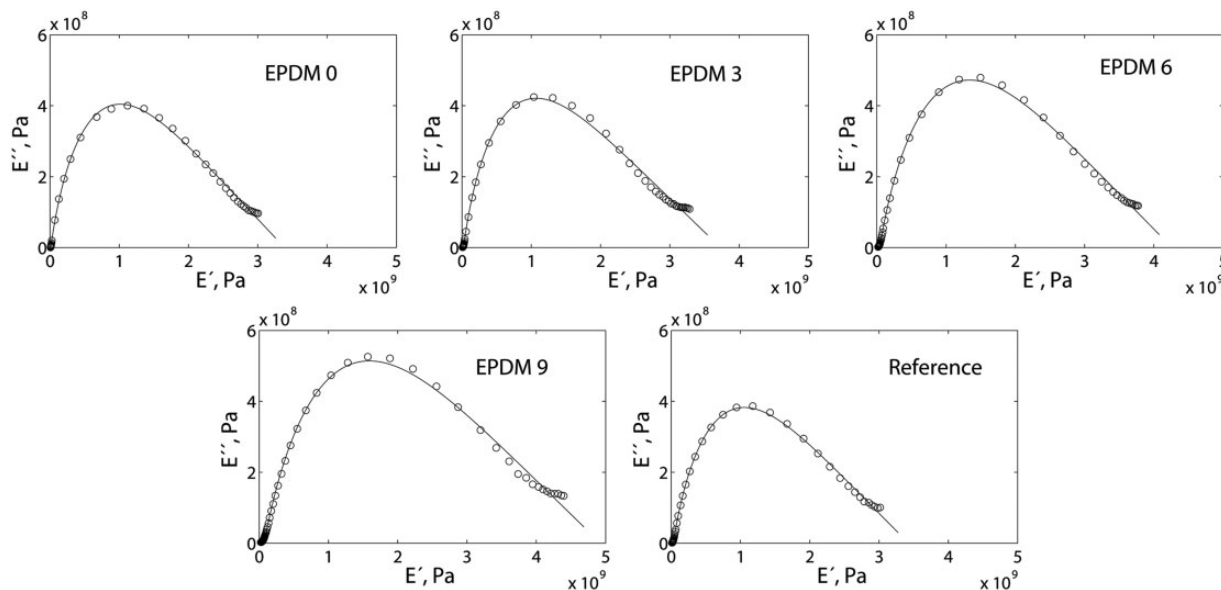
Calculated moduli values using Guth and Halpin–Tsai models were compared to the measured Young’s moduli of the compounds (Figure 4). It can be seen that the Guth’s model gives mathematically the best fit. One difference between the Halpin–Tsai and the Guth model is that the modulus predicted by the former for high filler loadings is fixed for a volume fraction of 1.00. Therefore, at higher filler concentrations Halpin–Tsai model predicts lower modulus values than measured values. Guth’s model does not have this anchoring and the results corresponds better the experimentally measured values.

The tensile stress softening of the compounds can be seen in the curves presented in Figure 5. The hysteresis, that is, stress–strain difference between consecutive stretch paths, was quantified and the results are shown in Table 4. It was found that the higher the

**Table 5.** Calculated values for the Havriliak–Negami parameters.

Sample	$\alpha$	$\beta$	$E_{\infty}$ , GPa	$E_0$ , MPa
EPDM_0	0.61	0.21	3.4	11
EPDM_3	0.62	0.19	3.7	21
EPDM_6	0.55	0.23	4.3	42
EPDM_9	0.51	0.23	4.9	73
Reference	0.57	0.22	3.4	29

CNT content, the greater the hysteresis loss, as expected for filled compounds, and leading to lower resilience. Several mechanisms have been suggested contributing to the large stress softening in CNT reinforced elastomers. The main causes include the breakage of the CNT filler network during the first extension, the reduction of the number of the elastically active polymer chains, which is typically called Mullins effect in CB filled systems, and the changing orientation of the CNTs. The latter one has been suggested being observable in an increase in the effective modulus.<sup>17</sup> In this context, it is interesting to discuss the observation that mechanical properties are arising from the reinforcing effect of the CNTs at lower concentrations when compared to conventional fillers like CB and silica,<sup>17</sup> as the formation of a percolating network will influence the stress–strain behavior. As illustration, for a CNT reinforced SBR/BR blend the electrical percolation limit was shown to lie between 1 and 2 phr for CNTs with an aspect ratio of 50–60.<sup>18</sup> Such low percolation limits have been confirmed for other elastomeric systems as well. Another example is SBR filled with different types of CNTs, where the percolation limits



**Figure 9.** Cole-Cole plots of (a) EPDM\_0, (b) EPDM\_3, (c) EPDM\_6, (d) EPDM\_9, (e) reference. The values were obtained from dynamic mechanical thermal analysis of the rubber samples.

were less than 1 phr.<sup>19</sup> In the latter study, it was also noticed that besides the aspect ratio, the nature of the CNTs and their ultimately structural quality affect this limit as well.<sup>19</sup>

The extent of filler–filler interactions as measured by the Payne effect is shown in Figure 6. This effect can directly be correlated with the strength of the filler–filler network in a soft rubber matrix. It is measured by calculating the difference between the storage modulus at low strain (maximum value) and at high strain. It is observed that the strain dependence on directly mixed compounds is identical to the correlation measured for the masterbatch-diluted material, indicating a similar filler–filler network structure.

Based on the TEM imaging (Figure 7), both, the EPDM\_6 and the directly mixed reference, contained well-dispersed CNTs as well as agglomerates. From direct TEM analysis, calculated average aspect ratios were similar to the masterbatch and directly mixed materials,  $25 \pm 11$  ( $n=212$ , EPDM\_6) and  $26 \pm 14$  ( $n=229$ , reference), respectively. Thus, the mixing method did not affect the aspect ratio. The aspect ratio was also determined by the equations described by Guth (equation (1)), and verified with Halpin–Tsai equation (equation (2)).

The aspect ratios obtained from the fitting were:  $L/d=25$  from the Guth equation,  $L/d=116$  according to the orthotropic Halpin–Tsai equation whereas the initial aspect ratio given by the supplier was 158. Thus, it seems that the CNT tubes are broken during the mixing of the compounds resulting in a lower aspect ratio. It is also possible that the modeling describes mainly the length of the effectively reinforcing sectors

of the CNTs rather than the actual length. Moreover, it is interesting to note that the value obtained by the Guth equation resembles the values determined directly from TEM images.

Based on the DMTA measurements ( $\tan \delta$  curves shown in Figure 8), only small differences were found between the glass transition temperature ( $T_g$ ) values of the different compounds. The  $T_g$  values based on the  $\tan \delta$  curve of all compounds are found to be similar  $\sim -48^\circ\text{C}$ .

According to the fitting of the Havriliak–Negami equation (equation (3)) to the data obtained by dynamic mechanical analysis we have followed the procedure as described by Szabo and Keough.<sup>12</sup> The fitting yielded the values of the Havriliak–Negami parameters  $\alpha$ ,  $\beta$ ,  $E_\infty$ , and  $E_0$  and is shown in Table 5. The graphical representations of the fitted curves together with experimental data are also shown in Cole–Cole plots<sup>20</sup> (Figure 9). The parameters show a good fit for  $\tan \delta$  on the high frequency end, but deviate from the experimental values at the low frequency end.

With the increase of the CNT content  $\alpha$  value is lower (asymmetric nature of the Cole–Cole plot), but there is no clear effect on the  $\beta$  value (the broadness of the Cole–Cole plot). This indicates that the low frequency behavior, that is, intermolecular motion, of the CNT filled EPDM is affected by the CNT content (change in  $\alpha$ ), while the high frequency behavior, that is, small scale molecular motions, is not affected.<sup>13,17,21</sup> Thus, presence of small amount of CNT affects the molecular dynamics in the rubbery region. The  $E_0$  and  $E_\infty$  values increase when raising the CNT content. The directly mixed reference has  $\alpha$  and  $\beta$  values close to the masterbatch mixed

compound EPDM\_6, but the  $E_0$  and  $E_\infty$  are notably lower. Thus, based on the Havriliak–Negami parameters, it can be said that presences of small amount of CNTs affect the molecular motion during the glass to rubber transition of the polymer chains.

## Conclusions

The masterbatch mixing process allows the preparation of the compounds with the high level of CNTs which can be embedded in the continuous carrier setting free CNTs to a much smaller extent in the second step, the dilution to the desired concentration. The preparation of the CNT-elastomer composites is thus more controlled and less problematic in comparison with the conventional one-step mixing process. Furthermore, weighting and handling of the neat masterbatch is easier and filling of the mixer takes place faster and is cleaner.

The extra mixing step of masterbatch mixing does not negatively influence the properties of the composite compared to the direct mixing method: Based on the mechanical and thermal characterization, the properties of the masterbatch mixed compounds are very similar to what is obtained with direct mixing. Therefore, the masterbatch technique is useful to get better and healthier working environment.

Micromechanical fitting provided an estimation of the aspect ratio in the cured compound to be 25, which was supported by the TEM image analysis. This value is significantly lower than the original value of the CNTs indicating the breakage of the nanotubes during the mixing process. The filler–matrix and filler–filler interaction increase when the compound becomes more loaded, as seen in the Payne effect. Based on the Havriliak–Negami fitting with the data obtained from dynamic mechanical analysis, the CNT affects the molecular motion in the rubbery region.

## Declaration of Conflicting Interests

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