

Dynamic Mechanical Analysis of Rubber Mixtures filled by Carbon Nanotubes

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In this paper we observe dynamic mechanical properties of rubber mixtures – standard and CNT, where in the mixture CNT were dispersed nanoparticles – shape of carbon nanotubes (CNT). We used the testes apparatus by PerkinElmer “PYRIS Diamond Dynamic Mechanical Analyzer” for measuring mechanical properties. Dynamic mechanical analysis (DMA) is a technique used to study and characterize materials. It is the most useful for studying the viscoelastic behavior of polymers. A sinusoidal stress is applied and the strain in the material is measured, allowing one to determine the complex modulus. The temperature of the sample and the frequency of the stress are often varied, leading to variations in the complex modulus. Dynamic mechanical properties of tested mixtures are evaluated using frequency and thermal dependence. Dynamical tensile test we did during temperature program from 20 °C to 100 °C. We gradually applied frequencies 0.01 Hz, 0.5 Hz, 1 Hz, 10 Hz, 20 Hz and 50 Hz.

Keywords: DMA, Nanofillers, Storage Modulus, Loss Modulus, Complex Modulus

1 Introduction

Nanocomposites technology is a new era in polymeric materials. Rubber based nanocomposites are attracting considerable interest in polymer science research. Incorporation of different nanoreinforcements such as layered silicate clays, carbon nanotubes, nanofibers and silica nanoparticles into elastomers significantly enhances their mechanical, thermal, dynamic mechanical, and barrier properties along with noticeable improvements in adhesion, rheological and processing behavior [1], [2]. The presented work is devoted to the investigation of the single wall carbon nanotubes (SWCNT) influence on the dynamic mechanical properties of rubber mixtures. Due to their extremely high stiffness and aspect ratio with low density, carbon nanotubes as mechanically reinforcing fillers for polymers are extensively studied in the last years [3], [4]. The unique properties of CNT makes their superior compared to conventional fillers such as carbon blacks and silicas which require higher filler loading to boost the physico-mechanical properties of polymers. Compared with classic polymers, CNT-reinforced composites have shown dramatic improvement in stiffness, strength, and damping properties [5]. One of the issues in CNT-based elastomeric polymeric nanocompositions is how to achieve a homogeneous good dispersion of CNT in a polymer matrix to maximize the improvement of the different performance of the resulting composites. Solution mixing is one approach for processing polymer nanocomposites. The process of making rubber mixture/nanotubes divided into following processes: dispersion of nanotubes, dissolution of the rubber, mixing of Rubber with nanotubes solution, pressing the sample [6].

2 Material and methods

2.1 The Properties of Rubber Mixtures

By the term rubber mixture is understood the mixture of natural or synthetic caoutchouc with more ingredients, which are used to regulate its workability, allow vulcani-

zation and the final properties of vulcanizes are determined. Its quality is one of the basic assumptions of quality of rubber products. The particular parts of products have different functions and therefore the rubber mixtures are various. The final properties are influenced by lot of factors [7]. During evaluation the influence of factors on the dynamic mechanical properties it can be accentuate, that effects of some factors are linked with each other and it is not possible to expressly quantitative asunder. They can be divided to following groups [8]:

Chemical:

- volume and type of used caoutchouc, or combination of caoutchouc,
- stage of reticule and desperation filler,
- type of used additives,
- the nature of interaction of filler-filler and caoutchouc-filler,
- stage of mixture filling,
- distribution of stage in system,
- kind of used filler,
- interface between caoutchouc and filler.

Physical:

- viscoelastic properties of vulcanizates,
- the temperature of glassily transition,
- the measure conditions,
- the frequency, on which is measurement doing,
- the temperature of measurement,
- the amount of deformation during of measurement.

Application:

- conditions of vulcanizate exploitation (temperature of operation, surroundings, stage of loading).

From the material point of view the use of reinforcing

fillers gives the material unique properties, a combination of high elasticity with high strength. The addition of the filler to the polymer increases both modules G and E, according to a hydrodynamic effect. The filler polymer effects are determined by the structure of the filler and its interaction with a matrix. Fillers presence in the matrix also substantially influences transport phenomena of such composites [9], [10]. In this frame, utilization of nanotubes dispersed in polymers and mainly in rubber is encouraging for transport phenomena changes. Then technology of rubber mixtures filled by nanotubes is described in European patents [11], [12].

2.2 Carbon nanotubes – their properties and structure

Carbon nanotubes are molecules consist of area graphite, which are rolling to long roller closed on the both endings [13]. The main characteristics of carbon nanotubes are:

- roller shape,
- superlative slenderness ratio (long a few tens of μm / diameter lower than 2nm),
- characteristic set-up of hexagon with consideration on self axle, named chiralite,
- semiconductive or metallic behavior on considering chiralite,
- the possibilities of easy formation long roll caused by Van der Waals forces,
- the potential to chemical modification [14], [15], [16].

The list of physical or mechanical properties CNT shows, that they can throw which-ever concurrency in certain applications (Tab. 1).

Tab. 1 The list of physical or mechanical properties of nanotubes [17]

Properties	CNT	Comparison
Size	$d = (0.6 - 1.8) \text{ nm}$	Photolithography offers diameter bigger than 50 nm
Density	$1.33 - 1.4 \text{ g.cm}^{-3}$	Aluminium - 2.7 g.cm^{-3}
Tensile strength	45 GPa	Steel - approximately 2 GPa
Max. current density	1013 A.m^{-2}	Molten copper wires - 1010 A.m^{-2}
Heat-transmission value (20°C)	$6000 \text{ W.m}^{-1}.\text{K}^{-1}$	Diamond - $3320 \text{ W.m}^{-1}.\text{K}^{-1}$
Melting point	2800°C -vacuum, 750°C -air	Aluminium - 660°C on the air

2.3 Dynamic module of polymer

Dynamic mechanical analysis, or DMA, is a dynamic characterization technique that measures stress as a function of strain, or force as a function of displacement. Viscoelastic materials, like polymers, behave both like an elastic solid and a viscous fluid. DMA measures the viscoelastic properties under dynamic oscillatory (often sinusoidal) test conditions [18].

When dynamic stress is applied to the material and a resultant strain is measured:

- The phase difference δ , between the stress and strain waves is measured.
- The phase lag will be 0° for purely elastic materials and 90° for purely viscous materials.
- Viscoelastic materials will exhibit an intermediate phase difference.

Typical viscoelastic properties include the following parameters:

- The storage modulus E' is the elastic component and describes the sample's stiffness.
- The loss modulus E'' is the viscous component and is related to the sample's ability to dissipate mechanical energy through molecular motion.

- The tangent of phase difference $\text{Tan } \delta$ provides information on the relationship between the elastic and inelastic components.
- The complex modulus E^* equals stress divided by strain.
- When the complex modulus E^* and the measurement of δ are known, the storage modulus, E' , and loss modulus E'' , can be calculated.
- Storage Modulus E' measures the stored energy, representing the elastic portion.
- Loss Modulus E'' measures the energy dissipated as heat, representing the viscous portion.
- $\text{Tan } \Delta$ is simply a ratio between the two, loss/storage, or E''/E' [19], [20].

During cyclic compression, when a constant load is applied in a sinusoidal form on sample, the sample deforms sinusoidally. We look at the two extremes of the material behaviors, elastic and viscous. Variation in the strain with frequency is given as:

$$\varepsilon = \varepsilon_0 \sin(t\omega) \quad (1)$$

where:

ε_0 ...Amplitude of sinusoidal strain curve [-],

t ...Time[s],

ω ...Angular frequency [s^{-1}].

Stress corresponding to the strain loading is represented by:

$$\sigma = \sigma_0 \sin(t\omega + \delta)[Pa], \quad (2)$$

where:

σ_0 ...Maximum stress applied [Pa],

δ ...Phase lag between stress and strain [$^\circ$].

The phase and amplitude of the relevant portion of resulting spectra of stress are used to compute the storage modulus E' , loss modulus for material E'' .

Storage Modulus:

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos \delta [Pa], \quad (3)$$

Loss Modulus:

$$E'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta [Pa], \quad (4)$$

The tangent of phase $\tan \delta$:

$$\tan \delta = \frac{E''}{E'} [-] \quad (5)$$

The complex modulus is the rate of stress to strain under vibratory conditions and given as:

$$E^* = E' + iE'' [Pa] \quad (6)$$

3 Experimental part

Tab. 2 Chemical contains of rubber mixture standard 1 and CNT 1

Components	Dose in PHR	
	Standard 1	CNT 1
NR	100	100
N660	27.6	27.6
ZnO	2.1	2.1
Gumodex	8.3	8.3
Sulphur	2.7	2.7
Accelerator	0.7	0.7
CNT	–	1.63

In this paper we observe dynamic mechanical properties of rubber mixtures – standard 1 and CNT 1, where in the mixture CNT 1 were dispersed nanoparticles – shape of nanotubes. The samples were made two by two, where sample presented like standard was without nanotubes and sample presented like CNT 1 had identical contains, but with same quantity SWCNT, like is described in the table 2.

The process of making rubber mixture/nanotubes divided into following processes:

Dispersion of Nanotubes - This phase involves the dispersion of CNTs in a special solvent in order to disentangle the nanotubes that typically tend to cling together and form lumps, which become very difficult to process. This solution was further sonicated using a mechanical probe sonicator capable of vibrating at ultrasonic frequencies in order to induce an efficient dispersion of nanotubes.

Dissolution of the Rubber - This stage involves the dissolution of components rubber mixture in a suitable organic solvent. This mixture was stirred and kept for certain duration of time until components became uniformly dissolved in the solvent.

Mixing of Rubber with Nanotubes Solution - This is the final step in the melt preparation process and basically involves thorough mixing of the solutions prepared in the first and second stages, resulting in a solution that consists of a good blend of nanotubes in the rubber composite.

Pressing the Sample - The rubber mixture/nanotubes material was pressed using hot press and cut into standard samples.

We used the testes apparatus by PerkinElmer “PYRIS Diamond Dynamic Mechanical Analyzer“ for measure dynamic mechanical properties. Dynamical tensile test we did during temperature program from 20 $^\circ\text{C}$ to 100 $^\circ\text{C}$. We gradually applied frequencies 0.01 Hz, 0.5 Hz, 1 Hz, 10 Hz, 20 Hz and 50 Hz.

The basic parts of device for dynamic mechanical analysis (DMA) are two collinear arms. Arms are placed on special pivots, which are located in the middle of arms. Pivots are very exact torsion springs. The specimen is clamped in special holder between two collinear arms. The device is situated in thermostatic environment, which enable to isothermal measure and to measure during changing of temperature, usually from -150 to 500 $^\circ\text{C}$. The deformations of sample are caused by two opposed moments of the same size, which impact on opposite ends of the sample clamped to the clamp. By DMA we can characterize polymer material, its dependence of modulus or losing angle $\tan \delta$ on temperature, possibly on time at various frequencies. So we obtain basic information about mechanical properties, which are related to processability and applicability of product.

Comparisons of dependence E' , E'' , E^* and $\tan \delta$ on the temperature of the samples standard 1 a CNT 1 by various frequencies are in figures 1-6.

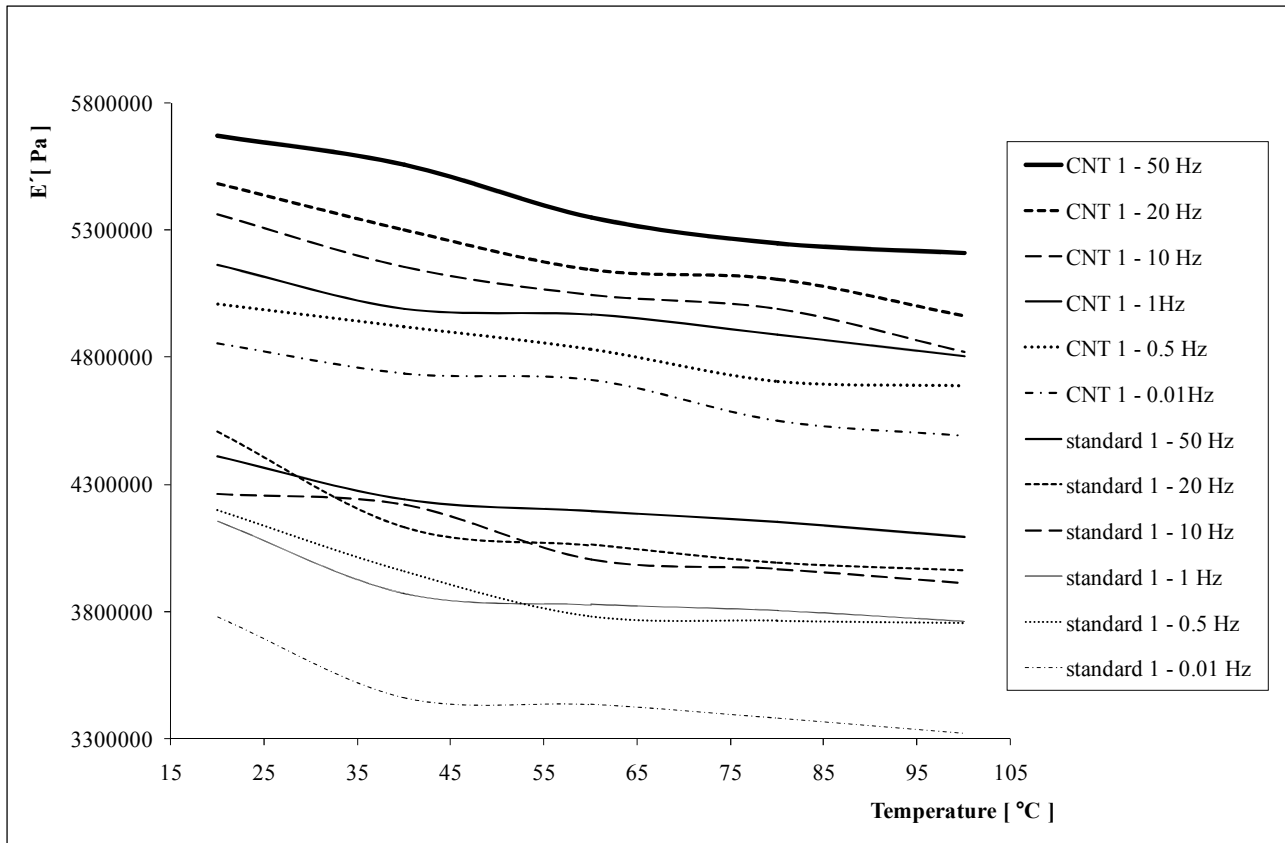


Fig. 1 Comparison of dependence E' on the temperature of the samples standard 1 a CNT 1 by various frequencies

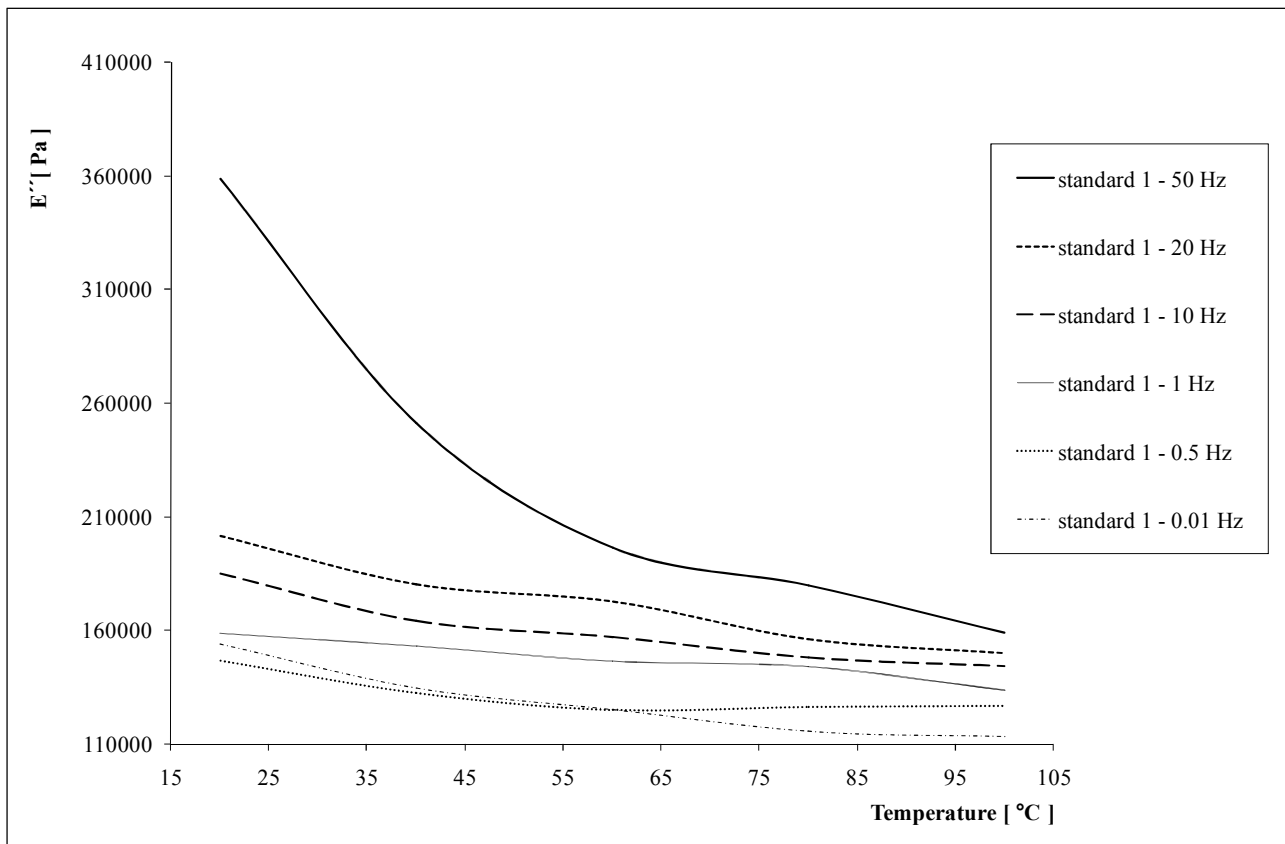


Fig. 2 Comparison of dependence E'' on the temperature of the sample standard 1 by various frequencies

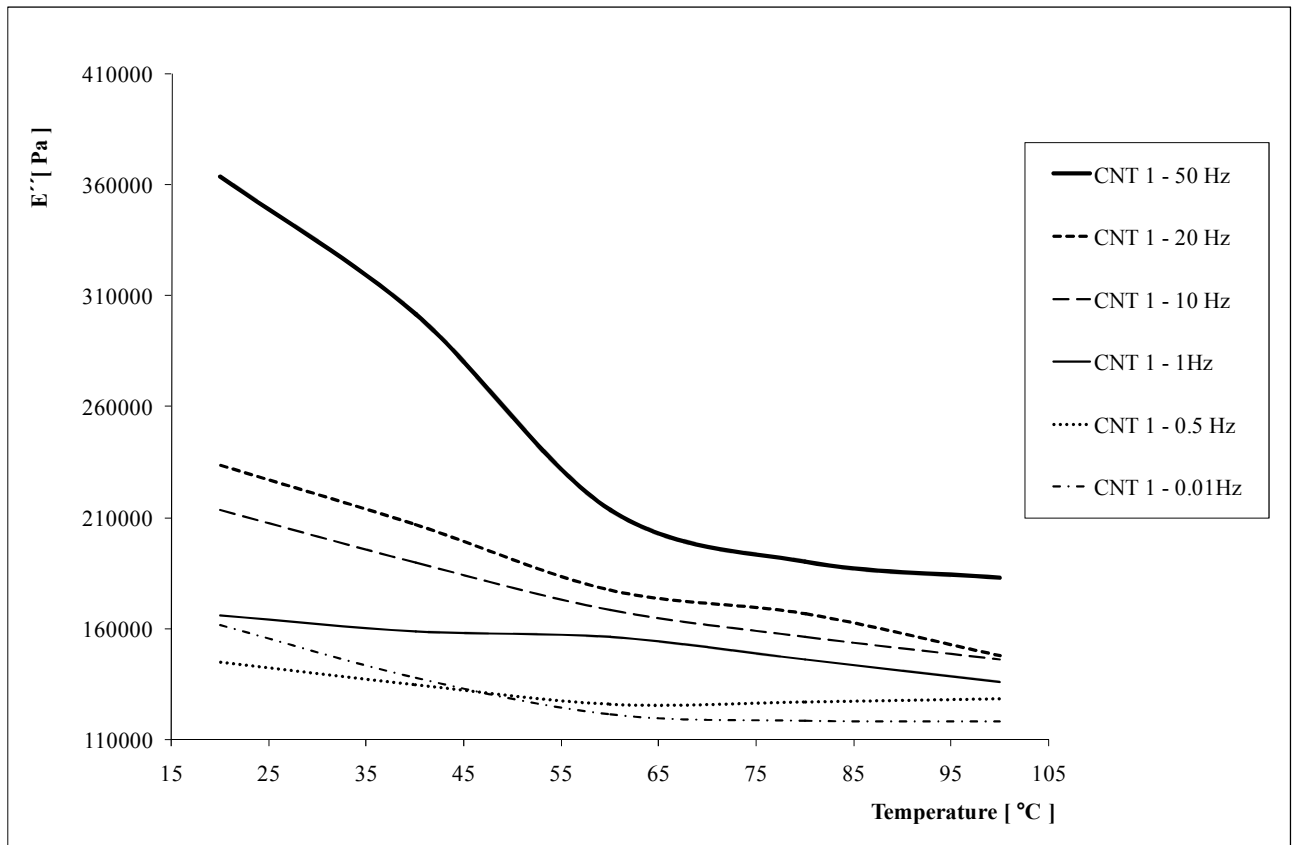


Fig. 3 Comparison of dependence E'' on the temperature of the sample CNT 1 by various frequencies

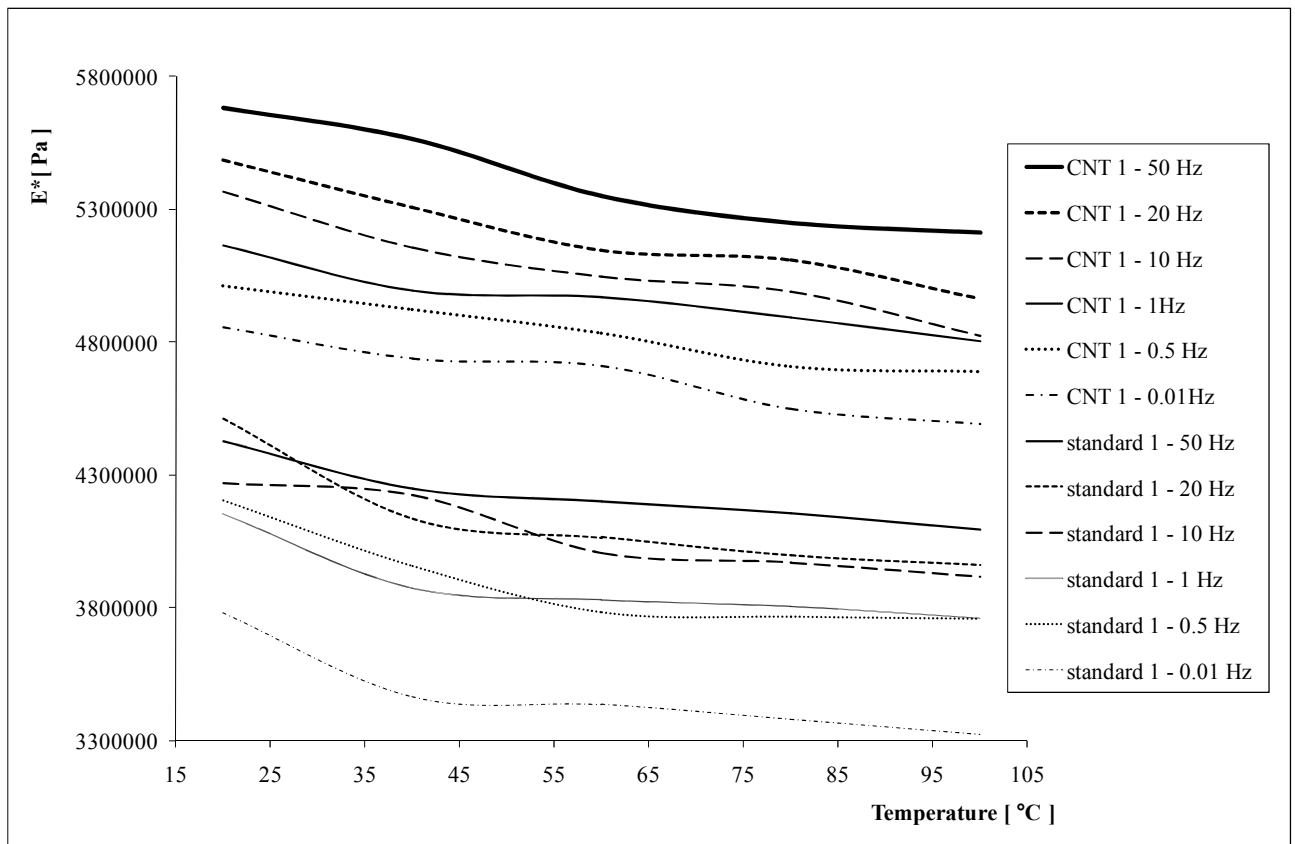


Fig. 4 Comparison of dependence E^* on the temperature of the samples standard 1 a CNT 1 by various frequencies

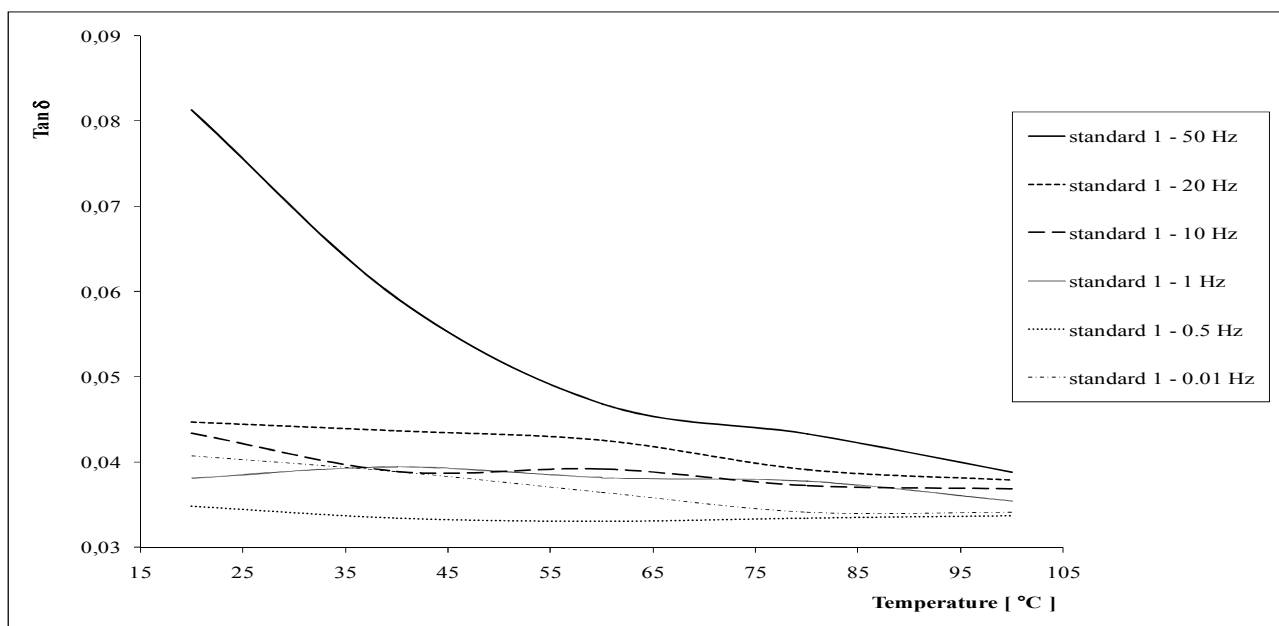


Fig. 5 Comparison of dependence $\tan \delta$ on the temperature of the sample standard 1 by various frequencies

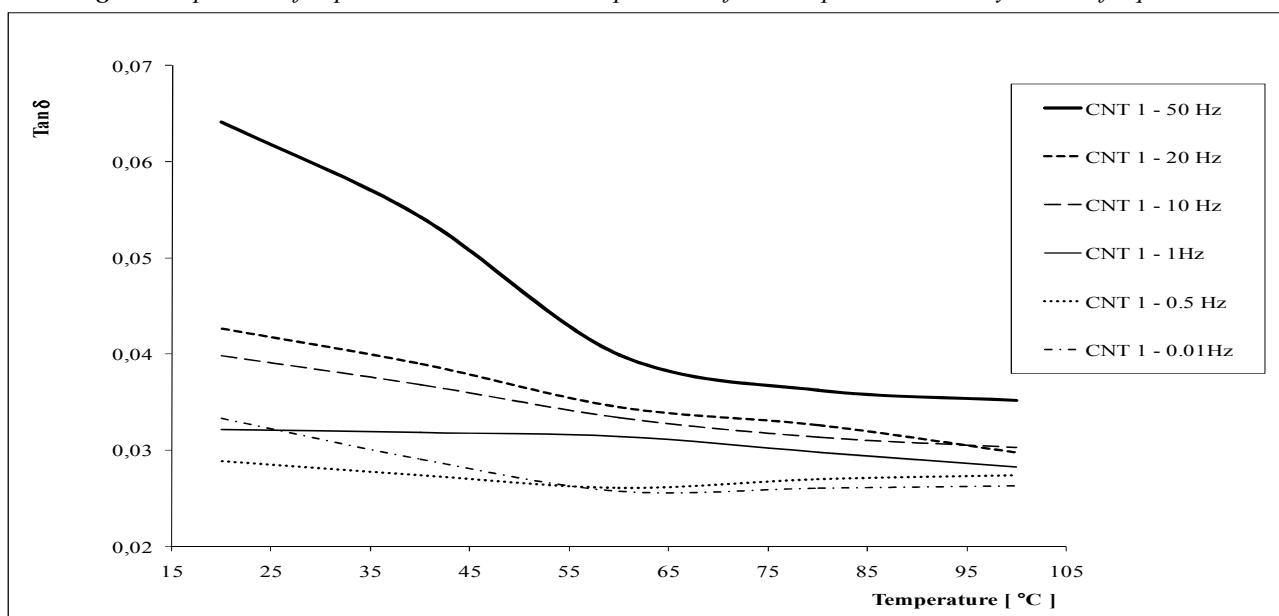


Fig. 6 Comparison of dependence $\tan \delta$ on the temperature of the sample CNT 1 by various frequencies

4 Results and discussion

The results of DMA were obtained for vulcanized samples only. From the graphic dependence of storage modulus E' (Fig. 1), loss modulus E'' (Fig. 2,3) and complex modulus E^* (Fig. 4) it can be seen, that values modulus are decreasing with increasing temperature and values of modulus are increased with increasing frequency.

From the dependence (Fig. 5,6) $\tan \delta$ on temperature it can be seen, that with increasing temperature values $\tan \delta$ are decreasing and with increasing frequency are values $\tan \delta$ increasing.

Rise of E' between samples 1 and CNT 1 (at the beginning of the temperature dependence) is approximately 26 % (Fig. 1). On the other hand, the presence of SWCNT does not substantially influence the value of E'' (it slowly

rises with the presence of SWCNT). The temperature dependence for lower frequency (0.01 Hz) is relatively flat (Fig. 2, 3) in all temperature spans under investigation. On the other hand, it is possible to see a relatively strong frequency dependence of E'' (approximately 125 percentage on the left side of the temperature dependence between values of E'' at frequencies 0.01 Hz and 50 Hz).

The results from the comparison samples 1 and CNT 1 (nanoparticles were dispersed in the samples in the shape of nanotubes):

- the values of storage modulus E' in the sample with nanotubes markedly increased - elasticity of sample was improved (Fig. 1),
- the values of loss modulus E'' did not changes significantly, so loss part of complex modulus did not change much (Fig. 2,3),

- the values of complex modulus E^* were increased - nanotubes improved mechanical properties of rubber mixture (Fig. 4),
- the values of $\tan \delta$ on the sample CNT 1 decreased, so adherence in wet and rolling-resistance force decreased (Fig. 5,6).

5 Conclusions

Recently CNT have been widely used to incorporate into rubber mixtures to develop high-performance composite materials. Dispersibility of CNT in rubber mixtures and the stress transfer from the matrix to CNT have significant effects on reaching ultimate mechanical properties for CNT/polymer composites. Mechanical processes to disperse CNT such as ultra-sonication have limited dispersing effect, and they are generally applied together with other dispersing processes to enhance the disperse effect of CNT. In addition to dispersibility of CNT in the matrix, the amount and orientation are two important factors which cannot be ignored. Optimum amount and high orientation of CNT should be considered in order to achieve excellent mechanical properties of CNT/polymer composite. CNT reinforcement increases the mechanical properties of rubber mixtures several times higher compared to neat rubber mixtures, which conforms that CNT are very effective fillers for rubber mixtures. However, the challenges the researchers should still face are how to optimize various factors in preparing CNT/polymer composite in order to reach its ultimate mechanical properties, and how to scale up from laboratory and thus realize mass production. Nanocomposites investigated within this thesis can be used in a wide range of industrial applications due to the combined properties of polymeric mixture and carbon-based nanofiller.

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