

## The influence of carbon nanostructures on tribotechnical characteristics of elastomers

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**Abstract:** Tribotechnical characteristics of elastomers based on SKI-3 isoprene rubbers and hybrid filler carbon black/carbon nanotubes (Taunit-M) produced by “Nanotechcenter” were studied in the paper. The content of carbon nanotubes in rubber mixtures was 0.5 wt. h. per 100 wt. h. of rubber. Asphalt concrete of grades I-II from a hot mixture of type A on bitumen BND60/90 was used as a counterbody. The experiments were carried out at rolling speeds from 60 to 80 km·h<sup>-1</sup> and normal loads of 3.0–3.5 kN. The measurement error did not exceed 2 %. It was experimentally shown that when the normal load varies, the dependence of mass wear on the rolling speed does not change its character. This behavior of elastomeric materials fully corresponds to the Archard wear model, according to which wear is directly proportional to normal load and rolling speed. An increase in the mass wear value of  $J_m$  with an increase in load is associated with an increase in adhesion in contact. The maximum difference in the mass wear value of  $J_m$  during tests at the speed of 80 km/h and the load of 3.5 kN for SKI-3 rubber and rubber/carbon filler reached 2 times. The use of carbon nanostructures reduced the amount of mass wear by almost 40 %. Therefore, the use of carbon black/carbon nanotubes filler for rubbers is a promising method for improving their tribotechnical properties.

**Keywords:** carbon nanotubes; elastomers; mass wear; rolling with slippage.

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## Влияние углеродных наноструктур на триботехнические характеристики эластомеров

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**Аннотация:** В работе изучены триботехнические характеристики эластомеров на основе каучуков SKI-3 и гибридного наполнителя технический углерод/углеродных нанотрубок (Таунит-М) производства ООО «НаноТехЦентр». Содержание углеродных нанотрубок в резиновых смесях составляло 0,5 масс. ч. на 100 масс. ч. каучука. В качестве контртела использован асфальтобетон I-II марок из горячей смеси типа А на битуме БНД60/90. Эксперименты проводили при скоростях качения от 60 до 80 км/ч и нормальных нагрузках – 3,0...3,5 кН. Погрешность измерений не превышала 2 %. Экспериментально показано, что при варьировании нормальной нагрузки зависимость массового износа от скорости качения не изменяет свой характер. Такое поведение эластомерных материалов полностью соответствует модели износа Арчарда, согласно которой износ прямо пропорционален нормальной нагрузке и скорости качения. Увеличение значения массового износа  $J_m$  с увеличением нагрузки связано с повышением адгезии в контакте. Максимальная разница величины массового

износа  $J_m$  при испытаниях на скорости 80 км/ч и нагрузке 3,5 кН для каучука СКИ-3 и каучука/углеродный наполнитель достигает 2 раз. Применение углеродных наноструктур позволило снизить величину массового износа почти на 40 %. Поэтому применение наполнителя технической углерод/углеродные нанотрубки для резин является перспективным методом улучшения их триботехнических свойств.

**Ключевые слова:** углеродные нанотрубки; эластомеры; массовый износ; качение с проскальзыванием.

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## 1. Introduction

To date, there is a problem of improving physical, mechanical and tribotechnical characteristics of elastomeric materials. One way to solve this problem is to use carbon nanostructures (schungite carbon and fullerene (0D), nanotubes (1D), graphene oxide (2D), graphite (3D)) as a reinforcing element [1]. The mechanical and physical properties of elastomeric materials such as tensile strength, tensile modulus, tear strength and hardness [2, 3] can be improved. However, few studies have been devoted to testing the tribological efficiency of these materials.

Since its discovery, graphene oxide (GO) has attracted a lot of interest from researchers around the world in various fields. It is used in biology, medicine, membrane technologies, used as fillers in polymer composite materials, etc. The use of nanocarbon fillers is currently focused on modifying their mechanical, electrical and/or optical properties of rubber compounds [4]. It should be noted that elastomers based on natural rubbers are a sensitive material to external factors (oxygen, ozone, sunlight, ultraviolet rays, and humidity) [5, 6]. The influence of fillers on rubber compounds has been carried out by several authors [3] to study the static and dynamic characteristics. The chemical and physical properties of nanocomposites have been significantly improved in a limited range [7–10]. Graphene is an atomic-scale cellular lattice consisting of carbon atoms [1], which has unique properties such as high specific area (about  $2630 \text{ m}^2 \cdot \text{g}^{-1}$ ), high modulus of elasticity (approximately 1.1 TPa) and high thermal conductivity ( $5000 \text{ W} \cdot (\text{m} \cdot \text{K})^{-1}$ ) [2]. These characteristics make it possible to speak of graphene as a promising material for various technologies, including biocompatible probing [4, 5].

In general, the use of GO as a nanofiller for strengthening elastomers is very important due to their limited use due to low strength properties [11].

At present, a lot of research has been devoted to strengthening of thermoplastic elastomers, since they are easy to process compared to conventional rubbers

[1]. As a rule, they are reinforced with inorganic fillers [12–14], including oxidized graphene [15, 16]. There are a number of studies in which an improvement in the mechanical characteristics of graphene-reinforced thermoplastics was shown [13, 17–26], and a number of micromechanical theories were developed [26]. To explain strengthening mechanisms in elastomer/graphene composite systems [14, 27, 28], the classical Gut-Gold theories [12], based on hydrodynamics, as well as more modern ones, such as the wedging theory [13, 29], which is mainly based on the percolation phenomenon were used. The corresponding theoretical analysis showed good agreement with the experimental results [13, 14, 18, 20, 23, 28]. However, some problems still remain unsolved when moving from microscopic to macroscopic scales in order to fully explain the mechanisms of mechanical amplification. In [30], the mechanisms of reinforcement of polymers by graphene nanoplates were established. Experiments have shown that for elastomers with a low shear modulus, the reinforcement efficiency of graphene nanoplates depends on the aspect ratio and volume fraction of the filler, and practically does not depend on its modulus.

A group of scientists led by Prof. Hato developed a viscoelastic material based on carbon nanotubes and elastomers [28], which exhibits unique physical and mechanical properties, however, rubber based on these elastomers had a reduced hardness (about 75 % of the base elastomer).

At Vyatka State University under the leadership of I.A. Mansurova the effect of carbon nanotubes on the physicochemical and physicomechanical properties of elastomers was studied [31–33].

All the results of the above studies showed the promise of modifying elastomers with carbon nanostructures, but there are very few studies of tribological properties [35]. In this regard, the purpose of this research is to study the effect of carbon nanotubes on the wear of elastomers during rolling with slip.

## 2. Materials and Methods

### 2.1. Materials

Rubbers based on SKI-3 rubbers were used as elastomer samples – elastomer material (EM) and nanostructured elastomer material (NEM), reinforced with a hybrid filler carbon black (TC)/carbon nanotubes “Taunit-M” (manufactured by LLC “NanoTechCenter”, Tambov) using the method presented in [32]. The TC was produced by JSC “Ivanovo carbon black and rubber”. Rubbers were obtained in the laboratory of rubber mixing and vulcanization of Vyatka State University, Kirov.

### 2.2. Research methods

To implement the study of the antiwear properties of elastomers under conditions of rolling friction with slippage along a circular path, a universal friction machine 2070 SMT-1 was used (Fig. 1).

For testing, we used the “disk-disk” scheme. The radial runout of the samples mounted on the lower shaft was measured with a dial indicator head and did not exceed 0.01 mm. The scheme enables to measure the moment of friction with sufficient accuracy to capture friction jumps.

Disks manufactured according to technological standards were used as the “disk” element. The

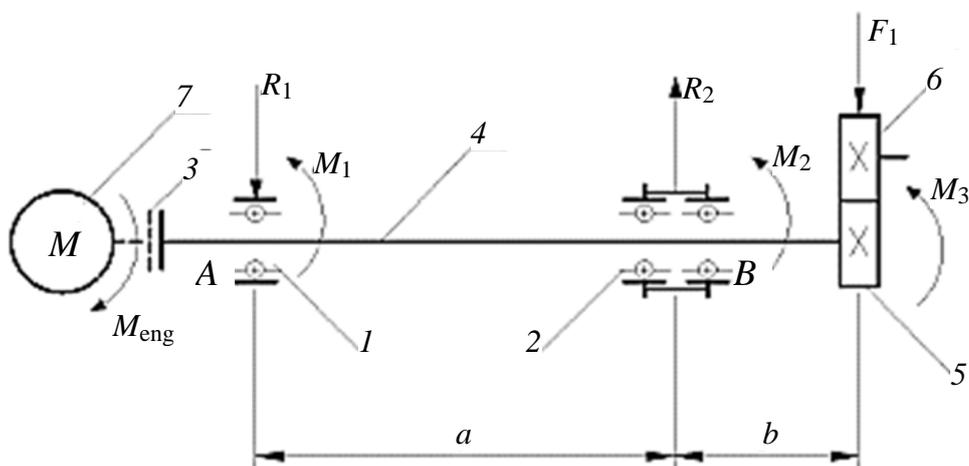
geometric characteristics of the samples used in the tests are shown in Fig. 2.

The main physicomechanical characteristics of elastomeric samples are presented in [36].

Samples with identical geometrical characteristics, made of asphalt concrete mixture, were used as a counterbody “disk”. Its characteristics are given in Table 1.

The temperature in the friction zone was recorded using a Fluke Ti400 thermal imager. The measurements were carried out in the range from 40–90 °C. A thermostat was not used. Testing of samples at each stage was carried out given the appropriate preparation: degreasing the elements of friction pairs, abrasion of samples until a stationary mode of rolling friction is obtained, measurement of linear dimensions and weighing of the sample before and after abrasion.

Measurements of the friction moment  $M_{fr}$  (N·m) were taken in a stationary mode. The samples were abraded at speeds from 60 to 80 km·h<sup>-1</sup>. Measurement errors are given in Table 2. The normal load varied from 3.0 to 3.5 kN, which corresponds to the actual load on the car wheel with an average weight of 1200 to 1400 kg. The mass was measured on an analytical balance VL-E134 with an accuracy of 0.00005 g.



**Fig. 1.** A diagram of measuring the moment of friction on the SMT-1 machine: 1, 2 – rolling bearings; 3 – sensor; 4 – shaft; 5, 6 – samples; 7 – electric motor

**Table 1.** Physical and mechanical properties of asphalt concrete

Material name	Modulus of elasticity $E$ , MPa	Density $\rho$ , kg·m <sup>-3</sup>	Poisson's ratio $\mu$
Dense asphalt concrete I-II grades from hot mix type A on bitumen BND60/90	5000	2350	0.20

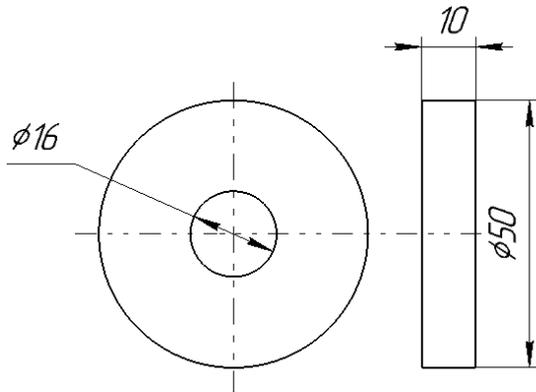


Fig. 2. Geometric characteristics of elastomeric samples

Table 2. Measurement errors

Measured value	Measuring range	Error
Friction path, km	1000	$\pm 0.001$
Normal load, kN	3.0–3.5	$\pm 0.01$
Rolling speed, $\text{km}\cdot\text{h}^{-1}$	60–80	$\pm 0.1$
Elastomer surface temperature, $^{\circ}\text{C}$	40–90	$\pm 0.1$

### 3. Results and Discussion

To assess the effect of rolling speed on the wear of elastomeric materials, a series of tests was carried out to determine the dependence of mass wear  $J_m$  on rolling speed. In order to approximate the experimental conditions to the real ones, we have chosen a range of speeds corresponding to the movement of passenger vehicles in the city (rolling speed  $v_k = 60\text{--}80 \text{ km}\cdot\text{h}^{-1}$ ). The friction path  $L$  amounted to 1000 km, the temperature in the contact zone varied from 22 to 65  $^{\circ}\text{C}$ . Two types of elastomers were tested: standard and nanostructured. The generalized data is shown in Fig. 3. It follows from the results obtained that the nature of the dependence of mass wear on the rolling speed under different loads does not change in the selected speed range. However, we note that the value of mass wear  $J_m$  during tests at a speed of 80 km/h and a load of 3.5 kN for a standard elastomer and a nanostructured elastomer differs by almost 2 times. This indicates an increase in the wear resistance of the elastomer due to the introduction of structural carbon filler. It should be noted that the use of CB/CNT in the structure of the elastomeric material led to a change in the temperature field in the contact zone, as well as to a

general decrease in the temperature of the elastomeric sample by 5–7  $^{\circ}\text{C}$ . This phenomenon can be explained by the high thermal conductivity of CNTs. Due to the increase in the temperature of the nanotubes, the temperature of the elastomer framework decreases; increase in the strength of bonds between chain molecules. This was confirmed in [37] and corresponds to the theoretical concepts of rubber elasticity physics [38].

In order to identify the influence of the magnitude of force on wear, laboratory tests were carried out with varying normal loads. Its value during the experiment varied from 3 to 3.5 kN. Based on the obtained results, histograms of the dependence of mass wear on the normal load were constructed (Fig. 4).

It should be noted that the presence of CB/CNTs in the structure of elastomeric materials leads to a decrease in the amount of mass wear at all applied static loads (by 40 % on average). The greatest decrease in the wear of the nanostructured elastomeric material in relation to the base material is observed at a vertical load  $P = 3.5 \text{ kN}$ , rolling speed  $v_r = 70 \text{ km}\cdot\text{h}^{-1}$ , the smallest at  $P = 3.0 \text{ kN}$ , rolling speed  $v_r = 60 \text{ km}\cdot\text{h}^{-1}$ . This behavior of elastomeric materials is fully consistent with the Archard wear model, according to which wear is directly proportional to normal load and rolling speed. An increase in the value of mass wear  $J_m$  with an increase in load is associated with an increase in adhesion in the contact.

It should be noted that the test results must be evaluated taking into account the constancy of the load. This means that the amount of wear in pneumatic tires will be affected by the internal air pressure, and in the studied samples it is absent.

To assess the anti-wear characteristics, we used the formula for determining relative wear:

$$J_m^{\text{rel}} = \frac{m^n - m^k}{m^n} 100\%, \quad (1)$$

where  $J_m^{\text{rel}}$  is the relative mass wear at a fixed normal load, %;  $m^k$  is the final mass of the sample at a fixed normal load,  $\text{mg}/1000 \text{ km}$ ;  $m^n$  is the initial mass of the sample at a fixed normal load,  $\text{mg}/1000 \text{ km}$ . The relative wear value was used to evaluate the wear resistance of nanostructured elastomeric materials in a given range of speeds and normal loads. According to our data, the increase in relative wear for a nanostructured elastomer at a fixed load is non-linear (Fig. 5).

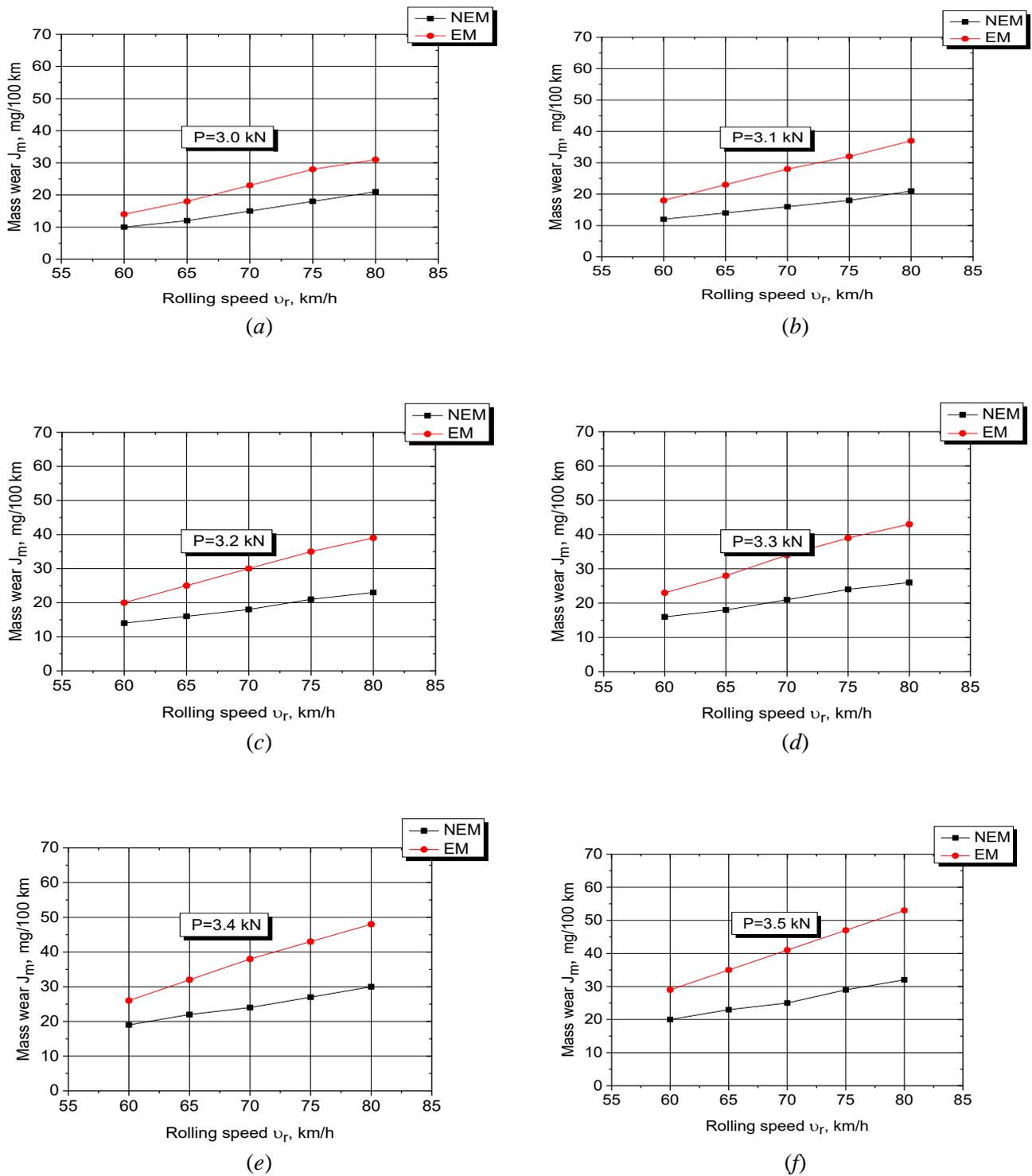
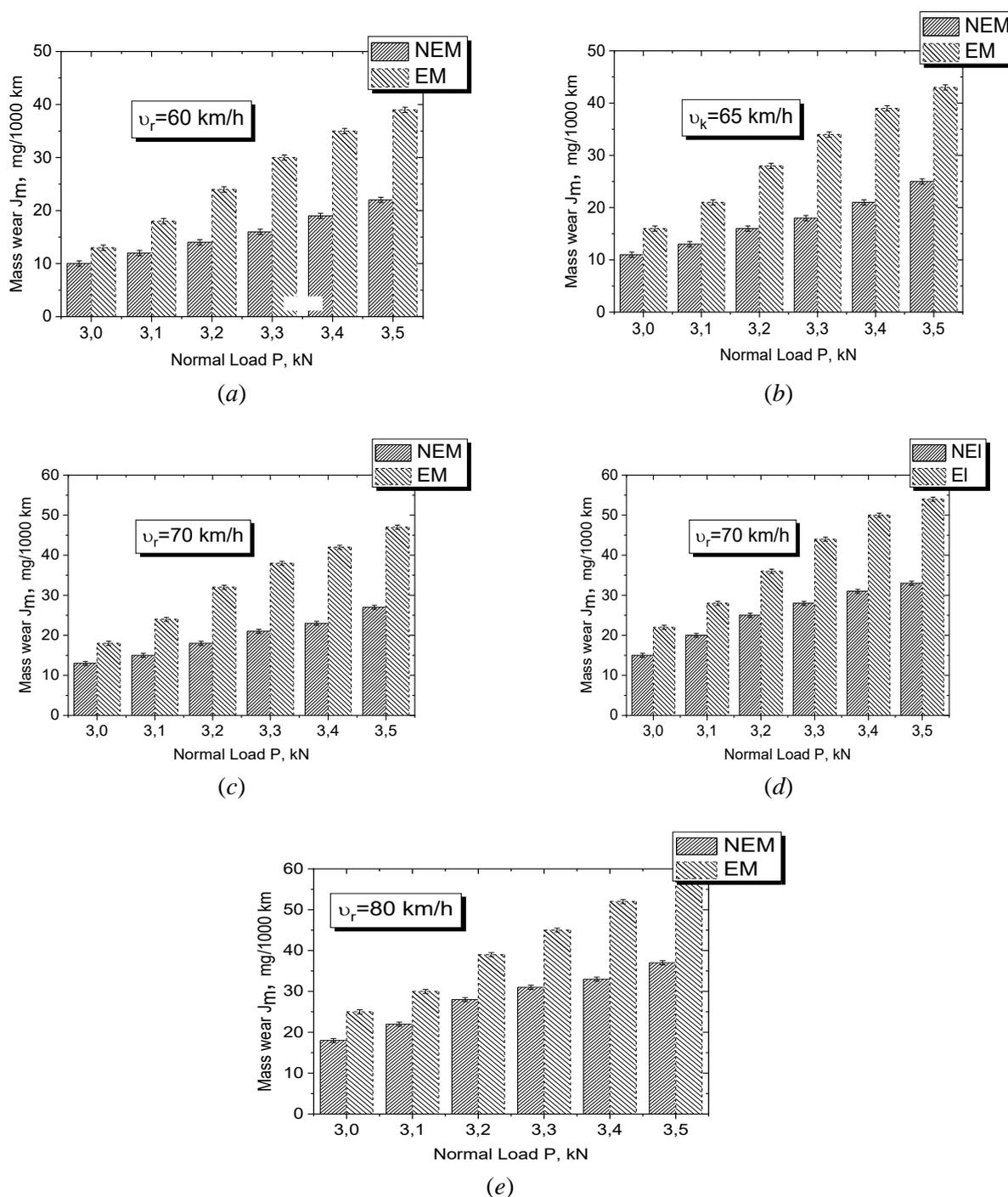


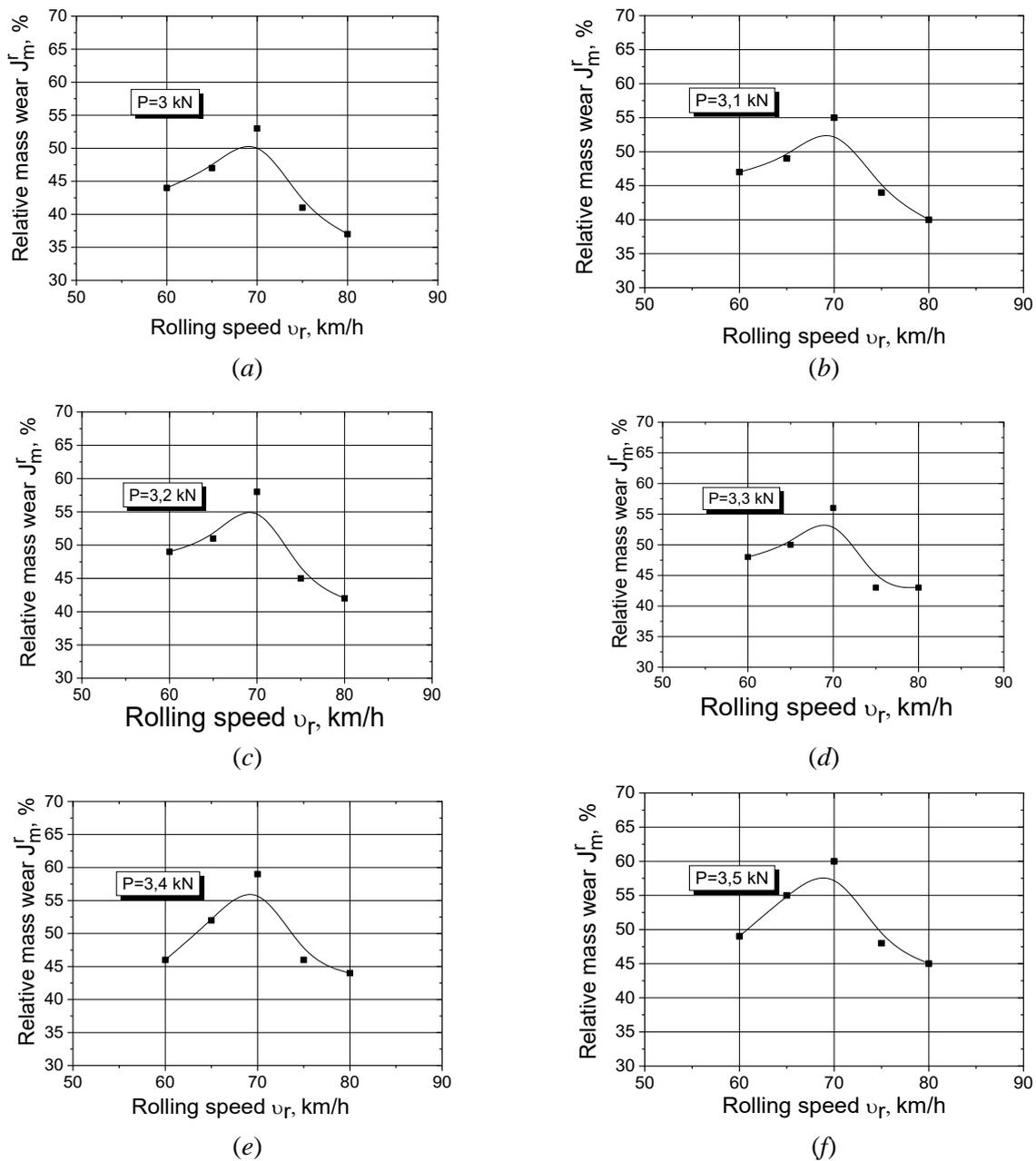
Fig. 3. Dependence of mass wear  $J_m$  on the rolling speed  $v_r$  under a constant load



**Fig. 4.** Histograms of the dependence of mass wear  $J_m$  on the magnitude of the normal load:  $a$  – rolling speed ( $v_r = 60$  km·h<sup>-1</sup>);  $b$  – rolling speed ( $v_r = 65$  km·h<sup>-1</sup>);  $c$  – rolling speed ( $v_r = 70$  km·h<sup>-1</sup>);  $d$  – rolling speed ( $v_r = 75$  km·h<sup>-1</sup>);  $e$  – rolling speed ( $v_r = 80$  km·h<sup>-1</sup>)

With an increase in the rolling speed from 60 to 70 km·h<sup>-1</sup>, the relative mass wear increases from 44 to 53 %, however, a further increase in speed leads to a gradual decrease to 37%. The data obtained indicate that a change in the composition of elastomers leads to an increase in wear resistance

from the region of low rolling speeds (60–70 km·h<sup>-1</sup>) to the region of high speeds (75 km·h<sup>-1</sup> or more). This means that the use of nanostructured elastomers will increase the resource of tread rubber and reduce the cost of purchasing a new set of pneumatic tires.



**Fig. 5.** Dependence of the relative mass wear  $J_m^{OTH}$  on the rolling speed  $v_k$  at constant normal load  $P$  for samples of nanostructured elastomers:  $a - 3$  kN;  $b - 3.1$  kN;  $c - 3.2$  kN;  $d - 3.3$  kN;  $e - 3.4$  kN;  $f - 3.5$  kN

#### 4. Conclusions

The production of automobiles is growing every year, so is the production of component parts, including pneumatic tires. Elastomeric materials used in the production of tires differ in their physical, mechanical and tribotechnical properties. One of these properties is abrasion resistance, i.e. wear resistance.

The paper shows that the dependence of mass wear on the rolling speed does not change its

character when the normal load is varied. The maximum difference in mass wear  $J_m$  during tests at a speed of  $80 \text{ km}\cdot\text{h}^{-1}$  and a load of  $3.5 \text{ kN}$  for a standard elastomer and a nanostructured one reaches 2 times. The use of nanoparticles in the structure of elastomer materials leads to a decrease in mass wear by almost 40%. This is due to strengthening of the elastomer framework by bonds with nanotubes. Also, their use will increase the wear resistance of elastomers and make it possible to use them at high speeds ( $75 \text{ km}\cdot\text{h}^{-1}$  or more).

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## 6. Conflict of interests

The authors declare no conflict of interest.

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