Electrical, mechanical and dynamic properties of ternary composites from acrylonitrile butadiene rubber and conductive fillers

ABDULLAH G AL-SEHEMI^{1,2}, AHMED A AL-GHAMDI³, NIKOLAY T DISHOVSKY^{4,*}, PETRUNKA A MALINOVA⁴, NIKOLAY T ATANASOV^{5,6} and GABRIELA L ATANASOVA^{5,6}

¹Research Centre for Advanced Materials Science (RCAMS), King Khalid University, Abha 61413, Saudi Arabia

²Department of Chemistry, College of Science, King Khalid University, Abha 61413, Saudi Arabia

³Department of Physics, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia

⁴Department of Polymer Engineering, University of Chemical Technology and Metallurgy, Sofia 1756, Bulgaria

⁵Department of Telecommunications, Faculty of Telecommunications and Management, University of Telecommunications and Post, Sofia 1700, Bulgaria

⁶Department of Communication and Computer Engineering, Faculty of Engineering, South-West University 'Neofit Rilski', Blagoevgrad 2400, Bulgaria

*Author for correspondence (dishov@uctm.edu)

MS received 1 August 2018; accepted 11 February 2019; published online 5 June 2019

Abstract. This paper presents comparative investigations on dual and ternary composites based on nitrile butadiene rubber. These composites were filled with carbon black and nickel powder at various ratios with each filler or with a combination of both. The focus of this study is on the electrical, mechanical and dynamic properties of the materials as influenced by the loading rate, applied pressure and bending degree have on the specific volume electrical resistivity. The investigations of the dynamic properties view the effect that the amount and chemical nature of the fillers have on the storage modulus and the tangent of the mechanical loss angle. It has been established that the specific characteristics of each of the fillers (particle size, specific surface, tendency to aggregate and agglomerate, interaction with the elastomeric matrix) have the greatest impact on composite properties. Scanning electron microscopy studies of the fillers and composites also confirm the results obtained.

Keywords. Ternary composites; nitrile butadiene rubber; conductive fillers.

1. Introduction

Recently, electrically conductive polymer composites have been of a high demand because of the increasing need for many applications such as electromagnetic interference shielding materials [1], self-regulated heating materials [2], pressure sensors [3], etc., which are produced using these materials. Conductive rubbers have been widely used [4,5] due to their properties such as flexibility, lightweight and the ability to absorb mechanical shocks. To effectively improve the electrical conductivity of rubbers, experiments have been performed with a variety of conductive fillers-e.g., carbon black (CB) and metallic powders (Ni, Al, Cu, etc.) [3,6,7]. The experiments have demonstrated the impact that filler properties (e.g., particle size, surface area, aggregate structure and surface activity), dispersed in the matrix [8] and rubberfiller interactions has on the electrical properties of conductive composites.

Unlike dual (rubber-metallic powder) systems, the properties of which are well studied, there are much less studies on the properties of ternary systems (rubber-CB-metallic powder) and on their comparison with the two-component ones loaded with fillers at the same degree [9]. Such types of studies are also of interest in view of the large difference in the chemical and structural properties of the fillers used, as well as regarding the possibilities to clarify the influence of the component ratio on the properties of the composite material.

The aim of the present study is to examine the properties of ternary (based on acrylonitrile butadiene rubber) composites containing a combination of conductive fillers including CB and nickel powder and to compare them with the properties of the composites containing each of the fillers individually at the same loading degree.

2. Experimental

2.1 Materials

The rubber matrix was Perbunan N 3310—nitrile butadiene rubber (NBR), a copolymer with 34% acrylonitrile content, specific gravity of 1.170 and Mooney viscosity ML(1 + 4) of 45 ± 5 at 100°C—produced by Lanxess.

The filler was conductive carbon black (CCB) Printex XE2-B—iodine adsorption 1091 mg g⁻¹, cetyltrimethylammonium bromide surface area—600 m² g⁻¹, Brunauer– Emmett–Teller surface area—1000 m² g⁻¹ and dibutyl phthalate absorption—403 ml per 100 g—produced by Orion Engineered Carbons.

The metallic filler was nickel powder—apparent density of $1.8-2.7 \text{ g cm}^{-3}$ and average particle size of 3-7 microns—produced by Alfa Aesar.

Local rubber enterprises provided the other ingredients such as *N-tert*-butyl-2-benzothiazolesulphenamide (TBBS), vulcanization accelerator, Vulkacit NZ and Vulkanox (from Lanxess), sulphur, zinc oxide (ZnO), stearic acid, processing oil and *N*-isopropyl-*N'*-phenyl-*p*-phenylene diamine, antiozonant, 4010NA.

2.2 Preparation of the samples

Table 1 presents the formulations of the NBR-based compounds (at phr) which comprise: acrylonitrile butadiene rubber-100, ZnO-3, stearic acid-2, processing oil (Petronet 620N)-10, TMQ-1, TBBS-1,5, sulphur-2, CCB Printex XE-2B and nickel powder (Ni) as fillers.

The compounds were prepared on a two-roll open laboratory mill $(L/D \ 320 \times 160 \ \text{mm}$ and 1.27 friction; slow roll speed of 25 min⁻¹). Test samples were vulcanized in the form of 15 × 15 cm large plates on an electrically heated vulcanization hydraulic press at 10 MPa and 160°C using a steel press. The vulcanization optimum was determined according to their vulcanization isotherms (ISO 3417:2010).

2.3 Vulcanization characteristics

Minimum torque (ML), maximum torque (MH), $\Delta M = MH - ML$, t_{90} (optimum vulcanization time), t_{S1} , t_{S2} (scorch times), tand@ML and tand@MH were obtained at $160 \pm 1^{\circ}C$ on an MDR 2000 rheometer (Alpha Technologies) according to ISO 3417:2002 using the vulcanization isotherms.

2.4 Mechanical properties

A tensile testing machine was used to determine the modulus at 300% of elongation. Tensile strength, relative elongation at break and residual elongation were determined at room temperature according to ISO 37:2002. Shore A hardness of the rubber composites was determined according to ISO 7619:2001.

2.5 Direct current electrical properties

2.5a Volume resistivity as a function of filler loading: The volume resistivity of the composites (ρ_v , Ωm) was measured according to the 2-terminal method and calculated using equation (1):

$$\rho_{\rm v} = R_{\rm v} S/h,\tag{1}$$

where R_v is the inter-electrode resistance (measured on a Wheatstone bridge allowing the device to adjust for 1 min or on a teraohmmeter when it was higher than $10^5 \Omega$); *h* is the thickness of the sample inserted between the electrodes measured by a Mitutoyo micrometer (0.001 mm) and *S* is the cross-section of the electrode, m².

2.5b *Effect of pressure on the volume resistivity*: To measure the effect of pressure on the resistivity, the pressure was changed in the range of 5–45 kPa by the weight of the measuring electrode used (see Section 3.3a), which was precisely calculated in advance, so the sample was subjected to pressures of 4; 10; 14.7; 20.6; 25.2; 32.1 and 42.6 kPa.

2.5c *Effect of bending on the volume resistivity*: An especially constructed testing set (figure 1) was used to study the resistivity as a function of mechanical deformation. The samples were subjected to permanent bending of 1-6% in the testing equipment which was connected to a teraohmmeter or a Wheatstone bridge.

2.6 Dynamic mechanical thermal analysis (DMTA)

Rectangular samples of the vulcanizates (10×25 mm, and thickness between 1 and 2 mm) were tested on a Dynamic Mechanical Thermal Analyser Mk III system (Rheometric Scientific). Their storage modulus (E') and mechanical loss angle tangent (tan δ) were determined at 5 Hz, under a single cantilever bending mode of 64 μ m, strain in the range of -80 to 80° C and at a heating rate of 3° C min⁻¹.

2.7 Scanning electron microscopy (SEM)

The electron microscopy images of the nickel powder, CCB and NBR-based composites were recorded on a JEOL ISM 5510 microscope. The SEM images of the nickel powder sample were obtained directly and those of CB from aqueous dispersion. Cross-sections were made from the vulcanizate samples following their treatment with liquid nitrogen. The

 Table 1. Formulations of the studied NBR-based compounds (in phr).

Composite	NBR 1	NBR 2	NBR 3	NBR 4	NBR 5	NBR 6	NBR 7	NBR 8	NBR 9
CCB/Ni amounts (phr)	15/15	25/25	30/30	30/0	50/0	60/0	0/30	0/50	0/60



Figure 1. Laboratory equipment for measuring the effect of bending on the volume resistivity. 1. Elastic textolite plate; 2. electrodes; 3. fixing bolt; 4. Teflon pad for fixing the distance; 5. steel axis setting the bending degree; 6. screw for fixing the bending degree; 7. contact sockets and 8. test sample.

samples thus prepared were covered with 24 carat gold in a JEOL JFC-1200 cathode-sputtering chamber.

3. Results and discussion

3.1 Vulcanization characteristics of the composites based on acrylonitrile butadiene rubber

The vulcanization characteristics of the studied composites are summarized in table 2.

The results in table 2 show that the chemical nature and characteristics of the fillers used to have an extremely important influence on the vulcanization characteristics of the rubber compounds. Therefore, there is an enormous difference in the characteristics of the ternary composites containing both types of fillers and the dual ones containing only CB or only nickel powder, respectively. Obviously, CB has the behaviour of an active filler strongly interacting with the rubber matrix, and the nickel powder is slightly active. In ternary composites with the increasing filler amount, all vulcanization characteristics increase with the exception of t_{S1} and t_{S2} (pre-vulcanization tendency), which decrease due to the influence of CB. The vulcanization parameters of the dual composites, although showing some similar trends in the observed changes with increasing loading, are characterized by very sharp changes in the composites with CB and minimal changes in nickel powder filled composites. It is also noteworthy that for ternary composites, the vulcanization optimum increases with an increase in the loading, whereas in the case of dual composites it decreases. The parameter is much better for composites with CB, and for those with nickel powder it is negligible. As seen, the combination of CB-nickel powder creates preconditions for retarding the vulcanization process, which in the dual composites does not occur. A similar effect has also been found by the authors [9] in the study on ternary systems filled with a combination of CB and silver powder. They have proven via X-ray studies that silver sulphide is

Table 2. Vulcanization characteristics of acrylonitrile butadiene rubber-based composites.

Composite	NBR 1	NBR 2	NBR 3	NBR 4	NBR 5	NBR 6	NBR 7	NBR 8	NBR 9
CCB/Ni amounts (phr)	15/15	25/25	30/30	30/0	50/0	60/0	0/30	0/50	0/60
ML, dN m	1.48	3.63	6.22	2.79	19.82	23.4	0.21	0.19	0.16
MH, dN m	14.92	26.91	33.68	19.60	60.05	69.2	5.67	5.45	5.13
$\Delta M = MH - ML$	13.44	23.28	27.46	16.81	40.23	45.80	5.6	5.26	4.97
t _{S1} , min:sec	1:47	0:53	0:30	0:05	0:05	0:03	6:51	6:35	6:28
t_{S2} , min:sec	2:09	2:13	0:59	1:20	0:07	0:05	7:11	6:25	6:07
t ₅₀ , min:sec	3:36	4:30	4:54	3:09	2:10	1:47	7:28	7:14	7:10
t90, min:sec	9:08	10:31	10:56	14:26	7:35	5:35	10:10	10:03	9:56
tand@ML	0.708	0.718	0.757	0.577	0.807	0.857	1.000	1.053	1.125
tand@MH	0.087	0.092	0.110	0.104	0.248	0.345	0.042	0.044	0.047

formed in the presence of CB, which evidently has a negative impact on the vulcanization time. It is believed that this can also lead to alterations in the other properties, such as electric ones.

It is clear from our SEM studies (figures 5 and 6) that in the absence of CB, the nickel particles agglomerate into large clusters encapsulated in the rubber matrix, whereas in the presence of CB no clusters are observed and the nickel particles are evenly dispersed in the matrix. Undoubtedly, in these two different cases, the filler–polymer matrix interactions between the particles and the ingredients of the vulcanizationaccelerator system are different. This leads to changes in the conditions of the vulcanization process and causes the changes observed in its characteristics.

3.2 *Physicomechanical parameters of the investigated vulcanizates based on butadiene-acrylonitrile rubber*

The physicomechanical characteristics of the vulcanizates are summarized in table 3.

The values of the physicomechanical parameters of the composites studied coincide completely with the expected fact that CB has the behaviour of an active filler, while nickel powder has that of an inactive one. The values of ternary and dual composites for M_{300} increase the tensile strength and the Shore A hardness increases with the amount of the filler while the relative elongation decreases. These changes are most pronounced in the CB filled composites, while in the nickel-based composites the changes are negligible or absent. In the ternary composite, the changes in properties with increasing fill rates are pronounced very well, but the performance is weaker than that of the dual composites containing CB. Undoubtedly, the reason is that half the amount of active carbon is replaced with the much less active one. Nevertheless, the structural changes in the composites observed by SEM can also be taken into account.

3.3 *Electrical properties of the investigated vulcanizates based on acrylonitrile butadiene rubber*

3.3a Dependence of specific volume resistivity on the filler concentration: The dependence of the specific volume resistivity of vulcanizates based on acrylonitrile butadiene rubber

on the concentrations of the fillers at room temperature and the applied pressure of 9.4 kPa is shown in figure 2. The values of the specific volume resistivity were determined at a relative error of $\pm 3\%$.

Acrylonitrile butadiene rubber is a semiconductor, whose specific electrical resistance is in the range of $10^8-10^9 \ \Omega m$. The conductivity of pure acrylonitrile butadiene rubber is predominantly electronic, because nitrile groups are located in the side chains of its macromolecules. The nitrogen atoms of these nitrile groups have the ability to exchange electrons with each other *via* a hopping mechanism. Thus, the electrical conductivity occurs on the secondary circuits, which is determined by the number of nitrile groups.

As a rule, the addition of electrically conductive fillers (e.g., metal powders) to the elastomers increases the electrical conductivity of the resulting composites, but in this case (figure 2a) such an effect has not been observed. Generally, all three composites have a specific volume impedance of $10^8 \Omega$, which is identical to that of pure nitrile rubber. Hence, despite the high concentration of the filler, the electroconductivity of the composites is controlled by the elastomeric matrix. As seen from figure 2a, with an increase in the amount of nickel powder from 30 to 50 and 60 phr, the specific volume resistivity is almost unchanged since the differences in the values of $\rho_{\rm v}$ are below the measurement error limits. Nickel powder as a metallic conductor should ease the transport of electrons, but that does not occur. The reason is due to the relatively large size of the nickel particles, which in turn reduces the number of conductive particles capable of forming conductive systems. Due to the large size of the nickel particles around them, a thick elastomeric film is formed that encapsulates them and hinders the transport of electrons. The fact that the conductivity of composites filled with nickel powder at 30, 50 and 60 phr is controlled entirely by the rubber matrix indicating that the layer separating the filler particles from each other is quite thick. This increases the distance between the individual aggregates of the filler.

Figure 2b shows the dependence of the specific volume resistivity of NBR-based vulcanizates on the concentration of CCB. As the figure shows, all three composites filled with CCB at 30, 50 and 60 phr, respectively, are electrically conductive because CCB specific volume resistivity has values lower than $10^3 \Omega m$, while the composites filled with nickel

Table 3. Physicomechanical parameters of vulcanizates based on acrylonitrile butadiene rubber.

Composite	NBR 1	NBR 2	NBR 3	NBR 4	NBR 5	NBR 6	NBR 7	NBR 8	NBR 9
CCB/Ni amounts (phr)	15/15	25/25	30/30	30/0	50/0	60/0	0/30	0/50	0/60
<i>M</i> ₃₀₀ , MPa	7.2	13.6	17.2	14.4	16.0	17.3	0.7	0.8	0.9
Tensile strength, σ , MPa	14.5	17.3	19.5	16.3	20.0	25.2	1.9	1.7	2.1
Relative elongation, $\varepsilon_{\rm rel}$, %	550	380	330	350	200	180	550	550	550
Residual elongation, $\varepsilon_{\rm res}$, %	10	10	10	20	15	10	10	10	10
Shore A hardness, rel. units	66	78	84	90	95	97	50	50	50



Figure 2. Dependence of the specific volume resistivity of NBR-based vulcanizates on the concentration of: (a) nickel powder, (b) CCB, and (c) nickel powder and CCB.



Figure 3. SEM images of nickel powder at a magnification of: (a) 10,000 and (b) 5000.

powder exhibit semiconductor properties. By increasing the amount of CCB from 30 to 50 phr, the specific volume resistivity decreases by more than 1 order, while at a further increase in the filler amount it is negligible. The composite filled with CCB at 30 phr is located in the area where the conductive structures have already been built and the electrical charges can quickly pass through the specimen. The dynamic equilibrium is established at filler concentrations of 50 and 60 phr. In all three composites, the conductivity of the filler, which has an ohmic character, prevails. On being introduced into the elastomeric matrix, CCB induces more electrons; thus, the exchange of electrons between the carbon particles becomes easier and faster than the exchange of electrons between the nitrogen atoms of the nitrile groups on the side chains of the rubber macromolecules. This is due to the formation of CCB particle aggregates which are chain-like and build conductive paths in the elastomeric matrix. At a certain content of CB, no matter whether the elastomer is a semiconductor or a dielectric, the conductivity of the composite is controlled by the phase of the filler.

The specific volume resistivity of NBR-based vulcanizates as a function of the concentration of the two fillers used is shown in figure 2c. The figure shows that with an increase in the amount of the combined filler, the specific volume resistivity decreases, i.e., the trend is the same as that for the composites filled with CCB only, but here the values of $\rho_{\rm v}$ are higher by about 1 order. Only the composite, which contains a combination of nickel powder at 15 phr and CCB at 15 phr, is referred to as a semiconductor, while the composites containing combined fillers at 50 and 60 phr are referred to as electrically conductive materials. When filled only with nickel powder, ρ_v of the composites is by about 5–6 orders higher than that of the ones filled with the combined fillers. Obviously, with the combination of the two fillers, the conductivity of the composites is controlled by the CCB phase and the charge transfer mechanism is the same as that for composites containing only CB. The differences in ρ_v values are due to the lower amount of CCB in the composites with the combined fillers. The explanations are confirmed by SEM studies of the fillers used and composites.

Figure 3 shows different crystalline structures formed in the investigated nickel powder having a layered structure. The nickel particles aggregate to form crystalline structures of the 'spiral rosette' type. The rosettes aggregate according to the forces of interaction between them and tend to have a pseudospherical shape. The spheres can also form tiles that build up domains of nanosized twins. The spiral growth of the nano twins forms the crystalline 'comb' structure.



Figure 4. SEM image of Printex XE-2B CB (cross-section).

A SEM image of Printex XE-2B CB used is shown in figure 4.

The micrograph shows the high structurality of CB expressed in the formation of chain aggregates, as well as their tendency to form agglomerates. The elementary particles are nano-sized.

Figure 5 shows SEM images of the investigated vulcanizates filled at 30 phr.

It is clear from figure 5a that the nickel aggregates are made of crystalline 'spiral-shaped' rosettes which retain their shape and dimensions after being loaded into the elastomeric matrix. The individual aggregates are coated with a rubber film, forming agglomerates which are located in separate groups along the matrix. This hinders the charge transport and correlates with the high values of the specific volume resistivity.

The micrograph (figure 5b) of the composite filled with electrically CCB at 30 phr is quite different. The magnitude of the carbon particles is much smaller than the size of the nickel particles, resulting in a significant increase in the number of carbon particles. The image shows clearly the structures of the filler, where its particles are in direct contact with each other, which results in their microscopic conductivity of an ohmic character. The elastomeric layers between the individual aggregates and agglomerates are very thin and therefore are overcome easily by the charge transfer. This explains the low values of the specific volume resistivity of the composites containing CCB as the filler.

With regard to the composite containing a combination of the two fillers at a total of 30 phr (figure 5c), the image is identical to that of the composite filled with CCB at 30 phr. In this case, one sees sporadically the aggregates and agglomerates of the nickel particles, which stand out in their larger dimensions, but in the elastomeric matrix the chain-like structures of the carbon particles, which act as conducting paths, predominate. The similarity in the morphology of the two composites also explains their values of specific volume resistivity and electrical conductivity, respectively.

Figure 6 shows SEM images of the composite filled at 60 phr.



Figure 5. SEM image of the composites based on acrylonitrile butadiene rubber at a filler amount of 30 phr: (a) nickel powder, (b) CCB and (c) nickel powder and CCB.



Figure 6. SEM images of composites based on acrylonitrile butadiene rubber filled at 60 phr with: (a) nickel powder, (b) CCB and (c) nickel powder and CCB.

Figure 6a clearly shows the nickel aggregates made up of a large number of particles of different sizes which are insulated from each other by a coating layer which provides contact resistance between them. In addition, the aggregates themselves are encapsulated with an elastomeric layer and are located in the matrix itself on separate islands remote from one another. This greatly impedes the charge transfer and blocks the high electrical conductivity of the nickel powder. In the composite filled with CCB at 60 phr (figure 6b), the location of the CB particles in the elastomeric matrix is identical to that in the composite filled with CCB at 30 phr, with the difference that the clusters of carbon particles in the chain aggregates are larger and the distance between aggregates is smaller. This facilitates the transport of electrons and $\rho_{\rm v}$ decreases, but to a lesser extent because the distance between the particles cannot be reduced to infinity and a dynamic equilibrium is established. The morphological structures of the carbon particles that build up the conductive paths predominate in the composite filled with nickel powder and CCB at 30 phr (figure 6c) and their phase controls the electrical conductivity of the vulcanizate. Here too, the aggregates of nickel particles have no relation to the conductive paths. Due to the CCB filling rate which is lower, if compared to that of the composite in the previous figure, the distance between the carbon particles and their aggregates is greater, resulting in the higher value of ρ_v .

The SEM images reveal that unlike the particles of nickel powder, CCB particles and aggregates are well dispersed in the elastomeric matrix in all composites loaded with this filler.

The explanations made of the electrical properties of the investigated rubber composites based on the results of the SEM images look the most probable and are in correspondence with the experimental results obtained.

3.3b *Dependence of the electrical resistance on the pressure applied*: The pressure dependences of the specific volume resistivity of the vulcanizates studied are presented in figure 7.

As seen from figure 7a, when the pressure increases to 20 kPa, the specific volume resistivity of the investigated vulcanizates decreases, whereas at NBR-1 and NBR-7 it is



Figure 7. Pressure dependence of the specific volume resistivity of NBR-based composites filled at: (a) 30 phr, (b) 50 phr and (c) 60 phr.

almost unchanged and at NBR-4 it continues smoothly and decreases slightly. With the filled elastomers, the application of pressure to the sample results in thinning of the elastomeric layers between the individual particles of the filler, which relieves the movement of the charge carriers and leads to a decrease in the resistivity. In the present case, this thinning of the elastomeric layers is most significant in the composite which contains CCB at 15 phr and nickel powder at 15 phr, probably due to better dispersion of the nickel powder in the rubber matrix in the presence of CB.

By increasing the filler amount (figure 7b and c), this tendency becomes less pronounced, with a relatively more noticeable change observed again in the composites containing a combination of the two fillers.

3.3c Dependence of specific volume resistivity on the applied bending deformation: The dependence of the specific volume resistivity of the investigated vulcanizates on the applied bending deformation is shown in figure 8.

According to figure 8, bending deformation has no effect on the specific volume resistivity of the composites under study. At bending, the mass of a sheet of vulcanizate suffers deformations of the intra-slipping layers (determined theoretically). The process is related to changes in the initial structure of the vulcanizate caused by the electrical resistivity output. Thus, electron transport becomes somehow easier while ion transition is hampered, and therefore the respective lower or higher resistance is affected.

As the obtained results show that the samples examined are not susceptible to the applied flexural deformations. This in turn does not result in a change in the thickness of the elastomeric film and thus facilitate the charge carrier transport, which ultimately does not result in a change in the resistance values for the composite.

3.4 *Effect of fillers used and the degree of filling on dynamic properties of the composites*

The measure of the elastic behaviour of a sample is the storage modulus (E') and the loss modulus (E'') is the measure of the viscous response of the materials. The ratio of the loss modulus to the storage modulus (E''/E') is the dynamic mechanical



Figure 8. Dependence of the specific volumetric resistance on the applied bending deformation for NBR-based composites filled at: (**a**) 30 phr, (**b**) 50 phr and (**c**) 60 phr.



Figure 9. Temperature-dependent storage modulus (E') for composites containing different chemical fillers at the same amount at: (a) 30 phr, (b) 50 phr and (c) 60 phr.

loss angle tangent (tan δ)—a measure of the energy dissipation in the material and an indicator of the viscoelasticity of the sample [10]. The storage modulus and the loss modulus of the composites studied were determined by DMTA.

Figure 9 shows the temperature dependence of the storage modulus of composites with different types of fillers in the temperature range of -80 to $+80^{\circ}$ C. The tested composites are grouped into three categories loaded: at 30 phr (figure 9a); at 50 phr (figure 9b) and at 60 phr (figure 9c).

The figures show similar dependencies and some differences. Above all, no noticeable changes in E' are observed in the temperature range of -80 to -10° C wherein the composites are in the glass state. During the transition from the glass-to-high-elastic state, which occurs around -10° C for all composites studied, E' begins to decrease sharply with a rise in temperature. The sharp decrease corresponds to the primary relaxation process associated with the glass-high elastic transition of the material [11]. The later drop of the modulus corresponds to an energy dissipation phenomenon observed during the relaxation process when tan δ passes through a maximum. Then E' values exhibit a plateau behaviour corresponding to the rubber state.

As seen from figure 9, in all cases the two-component composites containing only CB have the highest values of E', lower than the values of the ternary composites containing both types of fillers, and the lowest values are for the composites containing only nickel powder. With the increasing filler amount, E' values also increase, the effect being most pronounced in composites containing only CB, less in the ternary composites and negligible in the composites filled with nickel powder. It has already been mentioned in the discussion on the physicomechanical properties that CCB has an active filler behaviour, while the nickel powder is inactive. In the case of active fillers, as their quantity increases, the mobility of the polymer chains becomes increasingly limited, leading to an increase in E'. The storage modulus is also a measure of the reinforcing effect of single fillers. This shows that the reinforcing effect of composites containing only CCB and the combination of CCB/nickel, as well as the polymer-filler interaction is more pronounced compared to the composites containing only nickel. This is due to the difference in the size and specific surface of the fillers, their surface chemistry and their distribution in the polymer matrix. The higher specific surface area and the smaller particle size result in



Figure 10. Temperature dependence of the tangent of mechanical loss angle (tan δ) for composites comprising fillers of different chemical natures loaded at the same amount at: (a) 30 phr, (b) 50 phr and (c) 60 phr.

a stronger elastomer–filler interaction, a stronger reinforcing effect, a greater restriction of mobility of the macromolecules and higher E' values. With a strong rubber–filler interaction, the filler–filler interactions are less pronounced, allowing better dispersion of the filler and preventing the formation of its large aggregates. Obviously, nickel powder has the lowest impact on E', due to its large particle size, low specific surface area and high aggregation rate seen in SEM images (figure 3).

Figure 10 presents the temperature dependence of the tangent of mechanical loss angle for the composites studied.

There are no significant changes in tan δ values in the temperature range of -80 to -10°C. It is known that the peak value of tan δ corresponds to the glass transition temperature (T_g), i.e., it shows the transition temperature from the glassy to the highly elastic state of the composite. As seen from the figures, in dual composites filled with nickel powder, tan δ values at the transition in a highly elastic state are always the highest and practically do not change with

the increasing filler amount. In dual composites filled with CCB, as well as in the ternary composites, with the increasing filler amount tan δ values at the transition temperature in a highly elastic state decrease as the values of the ternary composites always remain higher than those of the composites, containing only CCB. The effect of decreasing values in ternary composites is also more pronounced (the values are reduced from 1.0 at 30 phr, 0.7 at 50 phr to 0.5 at 60 phr; in the dual carbon comprising composites, the respective values are 0.5, 0.3 and 0.25). The results correspond to the changes observed for scanning microscopy. The lower tan δ values correspond to a more limited degree of mobility of the polymeric macromolecules, respectively, to a stronger elastomer-filler interaction [12,13]. Obviously, these effects are the most pronounced in composites containing only CCB (the most active filler), lower in the ternary composites and the lowest in composites containing only nickel powder (the most inactive filler). After the transition into the highly elastic state, practically no differences in tan δ values have been observed.

4. Conclusions

The vulcanization, physicomechanical, electrical and dynamic properties of ternary composites based on acrylonitrile butadiene rubber filled with a combination of conductive fillers including CB and nickel powder were investigated and compared with the properties of the dual composites containing each of the said fillers at the same loading degree. The studies of electrical properties are focused on the influence of the loading rate, applied pressure and bending degree on specific volume electrical resistivity, while investigations of the dynamic properties involve the effect that the amount and chemical nature of the fillers have on the storage modulus and the tangent of the mechanical loss angle. It has been found that the specific characteristics of each of the investigated fillers (particle size, specific surface, propensity to aggregation and agglomeration, interaction with the elastomeric matrix) have the greatest influence on the properties of the composites. Of particular importance is the fact that in the presence of CB, the nickel particles are dispersed significantly better in the elastomeric matrix without the formation of aggregates and agglomerates, which to a great extent determines the changes in the properties of the ternary composites compared to those of the dual ones. SEM studies of fillers and composites also confirm fully and the results obtained are explained well.

Acknowledgements

The authors would like to acknowledge the support of King Khalid University for this research through a grant # RCAMS/KKU/006-18 from the Research Centre for Advanced Materials Science at King Khalid University, Saudi Arabia and that of the University of Chemical Technology and Metallurgy, Sofia, Bulgaria.

References

- Das N C, Khastgir D, Chaki T K and Chakraborty A 2000 Composites 31 1069
- [2] Feller J F, Chauvelon P, Linossier I and Glouannec P 2003 Polym. Test 22 831
- [3] Job A E, Oliveira F A, Alves N, Giacometti J A and Mattoso L H C 2003 Synth. Met. 135–136 99
- [4] Mahmoud W E, El-Lawindy A M Y, El Eraki M H and Hassan H H 2007 Sens. Actuator A Phys. 136 229
- [5] El Eraki M H, El-Lawindy A M Y, Hassan H H and Mahmoud W E 2006 Polym. Degrad. Stabil. 91 1417
- [6] Nasr G M, Osman H M, Abu-Abdeen M and Aboud A I 1999 Polym. Test 18 483
- [7] Sasikumar K, Suresh G, Thomas K A, John R, Natarajan V, Mukundav T et al 2006 Bull. Mater. Sci. 29 637
- [8] Yacubowicz Y and Narkis M 1990 Polym. Eng. Sci. 30 459
- [9] Thongruang W, Ritthichaiwong C, Bunnaul P, Smithmaitrie P and Chetpattananondh K 2008 Songklanakarin J. Sci. Technol. 30 361
- [10] Shaw M T and MacKnight W J 2005 Introduction to polymer viscoelasticity (New York: Wiley)
- [11] Angellier H, Molina-Boisseau S and Dufresne A 2005 Macromolecules 38 9161
- [12] Donnet J-B and Custodero E 2013 in *The science and technology of rubber* (4th edition) J E Mark, B Erman and C M Roland (eds) (Boston: Academic Press) p 383
- [13] Martens J E, Terrill E R, Lewis J T, Pazur R J and Hoffman R 2013 Rubber World 248 29