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A comparative study on the effect produced by fillers specifics on the dynamic mechanical and dielectric properties of natural rubber based composites

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ABSTRACT

This paper presents the results on the effect of specific characteristics of three completely different carbon black upon the dynamic mechanical and dielectric thermal properties of natural rubber based composites. It has been found that the size of carbon black particles, its specific surface area, respectively, as well as the ability of carbon black particles to form various aggregates and agglomerates affect both the dynamic mechanical and dielectric properties of the prepared composites. At the same concentration of all fillers studied the dynamic mechanical properties of the composites filled with high structure carbon black having super high specific surface area are much better than those of the composites filled with conventional carbon black. The same is valid for their dielectric permittivity (ϵ') values which are of about two-three orders higher.

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KEYWORDS

Natural rubber;
Nanocomposites;
Dielectric properties;
Dynamic properties;
Filler characteristics.

INTRODUCTION

Natural rubber (NR), produced by *Hevea Brasiliensis* is a general purpose rubber whose chemical structure is cis-1,4-polyisoprene^[1]. Possessing unique properties such as high tensile strength and ability to undergo a large elastic deformation the natural rubber elastomer is widely used in various applications, e.g. machine parts, construction parts, automotive parts etc.^[2].

With the development of electronic industry, some

special dielectric materials with high and/or low dielectric permittivity have been attracting notable attention of the academic and industrial circles. The dielectric properties of the insulative materials could be adjusted by dispersing different kinds of fillers into polymer matrices to afford polymer/filler composites.

The addition of fillers to the elastomers affects not only the dielectric properties but and the dynamic mechanical properties of the rubber composites obtained. The main characteristics of those composites are de-

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terminated by the size of the filler particles, their specific surface area, structure, coarseness, and surface activity^[3-5].

There has been an extensive study on the carbon black reinforcement of rubbers. The rubber molecules are absorbed on the carbon black particles surface, or included into its internal voids which results into a partial immobilization of the rubber and into an apparent increase in filler volume. Filler particles also form an agglomerated inter-particle structure which may be associated with specific elastic properties and a continuous breakup and rearrangement, finally leading to a strong nonlinear viscoelastic behavior^[6].

The effect that the size of carbon black particles has upon the dynamic mechanical properties of natural rubber based composites has been reported by Chuayjuljit

particles structure and their propensity to aggregate and agglomerate, the filler compatibility and interaction with the elastomer matrix. The comparison of the results from our investigations on those effects is reported in the current article.

EXPERIMENTAL

Characterization of the carbon black used

Three types of fillers having absolutely different specific surface area and structure were chosen for the experiments: furnace carbon black Corax N220, furnace carbon black Printex L6 and extra conductive black Printex XE-2B - all produced by Evonik Industries. The most important characteristics of the three types of fillers are summarized in TABLE 1.

TABLE 1 : Typical properties of the carbon black used

Carbon black	Iodine adsorption* mg/g	CTAB-surface area** m ² /g	BET surface area*** m ² /g	DBP-adsorption ml/100g	CDBP Adsorption ml/100g	Primary particle size, nm
Corax N 220	121	96	105	98	70	29-32
Printex L6	300	136	150	119	103	10-80
Printex XE-2B	1091	600	1000	403	370	5-20

et al.^[2]. The authors have established that the addition of carbon black affects the values of storage modulus (E') mechanical loss angle tangent ($\tan \delta$). The intensity of $\tan \delta$ peak decreases upon filling, especially with conventional N330 carbon black whose particle size is the smallest of all studied. The small particle size of the carbon black, its high specific surface area, respectively, favours its interactions with the rubber molecules. As a result, the chain flexibility is reduced and less mechanical energy could be transfer to the rubber molecules, consequently $\tan \delta$ decreases. However, literature data refer first of all to conventional carbon black (N330, N220, etc.). Recently new types of carbon black of unique properties have been developed. Their characteristics (iodine adsorption over 1000 mg/g, CTAB surface area 600 m²/g, BET surface area 1000 m²/g etc.) are much better than those of conventional carbon black.

With regard to tailoring the dynamic mechanical and dielectric thermal properties of composites it is worth studying how the former are affected by the mentioned above new carbon black and some of its properties, namely, by its particles size, specific surface area, the

The SAED images in Figure 1 present the amorphous structure of the three types of carbon black, the small particle size (<30 nm) and structurality of the fillers. As seen from TABLE 1 and Figure 1 the studied fillers differ entirely in their characteristics. The primary particles formed during the stage of the carbon black initial formation fuse together building up three dimensional branched clusters called aggregates. High structure carbon black exhibits a high number of primary particles per aggregate while low structure black has only a weak aggregation. These aggregates again form agglomerates linked by Van der Waals interactions. The empty space (void volume) between the aggregates and agglomerates usually expressed as the volume of dibutylphthalate (DBP) adsorbed by a given amount of carbon black is described by the term "structure" (or "structurality") of the carbon black. It is assumed that DBP adsorption reflects the total carbon black structure which comprises both aggregates and agglomerates, whereas the crushed DBP (CDBP) adsorption test eliminates loose agglomerates and easily destroyable aggregates. The images clearly show the tendency

of Printex L6 and Printex XE-2B to form large agglomerates in contrast to the conventional Corax N220 carbon black.

area, it was used at amounts lower than those of the other two types of carbon black.

The rubber compounds were prepared on an open

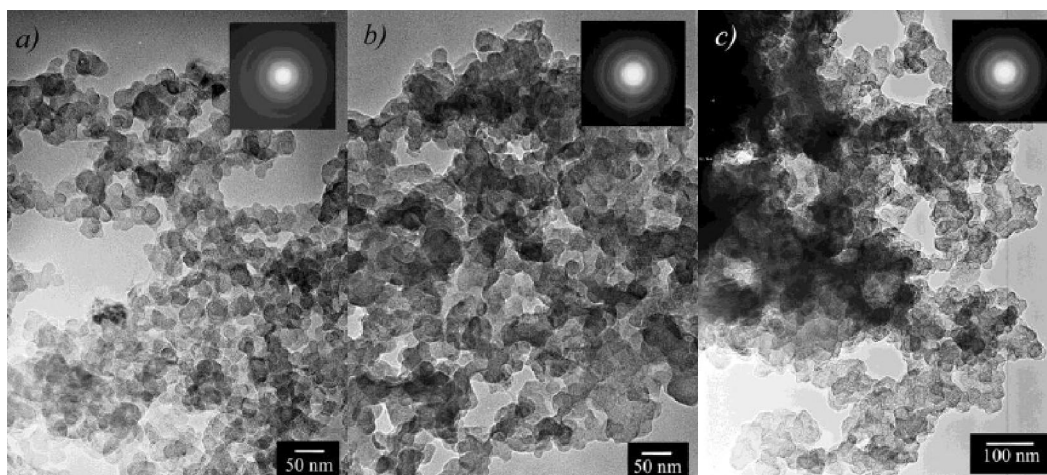


Figure 1 : TEM micrograph of carbon black used and micrograph in SAED regime (on the right): a) Corax N220, b) Printex L6, c) Printex XE-2B

Preparation and vulcanization of rubber compounds

The studies were performed on rubber compounds (in phr) summarized in TABLES 2, 3 and 4.

TABLE 2 : Composition of the studied rubber compounds comprising Corax N220 carbon black

	C1	C2	C3	C4	C5	C6
Natural Rubber (NR)	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
Stearic Acid	2	2	2	2	2	2
Carbon black Corax N220	0	10	20	30	40	50
TBBS ¹	0.8	0.8	0.8	0.8	0.8	0.8
Sulfur	2.25	2.25	2.25	2.25	2.25	2.25

¹TBBS – N-tert-butyl-2-benzothiazolesulfenamide

TABLE 3 : Composition of the studied rubber compounds comprising Printex L6 carbon black

	PL1	PL2	PL3	PL4	PL5	PL6
Natural Rubber (NR)	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
Stearic Acid	2	2	2	2	2	2
Carbon black Printex L6	0	10	20	30	40	50
TBBS ¹	0.8	0.8	0.8	0.8	0.8	0.8
Sulfur	2.25	2.25	2.25	2.25	2.25	2.25

¹TBBS – N-tert-butyl-2-benzothiazolesulfenamide

Since Printex XE-2B has a high specific surface

two-roll laboratory mill (L/D 320×360 and friction 1.27). The speed of the slow roll was 25 rpm. The experiments were repeated for verifying the statistical significance. The ready compounds in the form of sheets stayed 24 hours prior to their vulcanization.

TABLE 4 : Composition of the studied rubber compounds comprising Printex XE-2B carbon black

	PXE1	PXE2	PXE3	PXE4	PXE5	PXE6
Natural Rubber (NR)	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
Stearic Acid	2	2	2	2	2	2
Carbon black Printex XE-2B	0	5	7.5	10	15	20
TBBS ¹	0.8	0.8	0.8	0.8	0.8	0.8
Sulfur	2.25	2.25	2.25	2.25	2.25	2.25

¹TBBS – N-tert-butyl-2-benzothiazolesulfenamide

The optimal curing time was determined by the vulcanization isotherms, taken on an oscillating disc vulcameter MDR 2000 (Alpha Technologies) at 150°C according to ISO 3417:2002.

MEASUREMENTS

Dynamic mechanical thermal analysis

Dynamic properties (Storage modulus (E') and mechanical loss angle tangent (tan δ)) of the NR based vulcanizates were investigated using a Dynamic Me-

Full Paper

chanical Thermal Analyzer Mk III system (Rheometric Scientific). The data were obtained at 5 Hz frequency, 64 μm strain in the temperature range from -80 to 80°C using a heating rate of $3^\circ\text{C}/\text{min}$ under single cantilever bending mode. The dimensions of the investigated samples were as follows: width 10 mm, length 25 mm and the thickness measured using a micrometer varied between 1 and 2 mm.

Dielectric thermal analysis

Dielectric properties (Permittivity (ϵ')) of the NR based composites were investigated using Dielectric Thermal Analyzer (Rheometric Scientific) at 4 different frequencies (1 kHz, 10 kHz, 100 kHz and 1 MHz) in the temperature range between 20 and 100°C on a sample having a diameter approximately 32 mm and 1 mm thickness.

RESULTS AND DISCUSSION

Dynamic mechanical thermal analysis

The properties obtained by DMTA were the storage modulus (E') and the mechanical loss angle tangent ($\tan \delta$).

Figures 2, 3 and 4 present the temperature dependence of storage modulus (E') for the vulcanizates comprising different amounts of Corax N220 (Figure 2), Printex L6 (Figure 3) and Printex XE-2B (Figure 4).

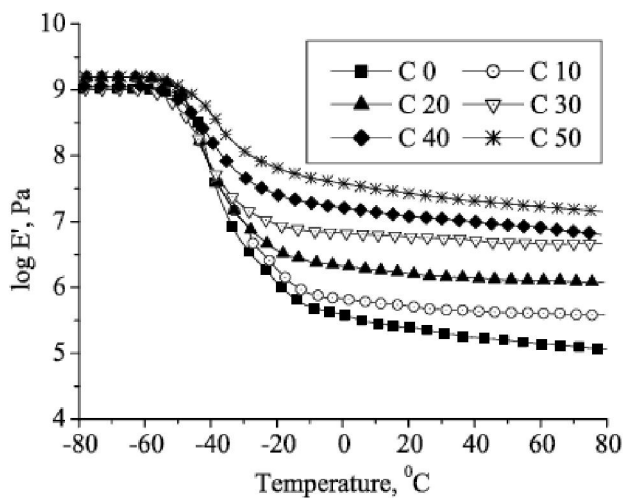


Figure 2 : Storage modulus (E') dependency on the temperature at various filler content for composites comprising Corax N220 carbon black

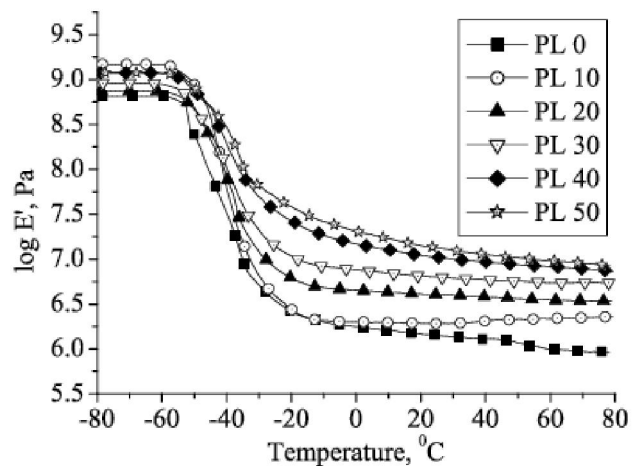


Figure 3 : Storage modulus (E') dependency on the temperature at various filler content for composites comprising Printex L6 carbon black

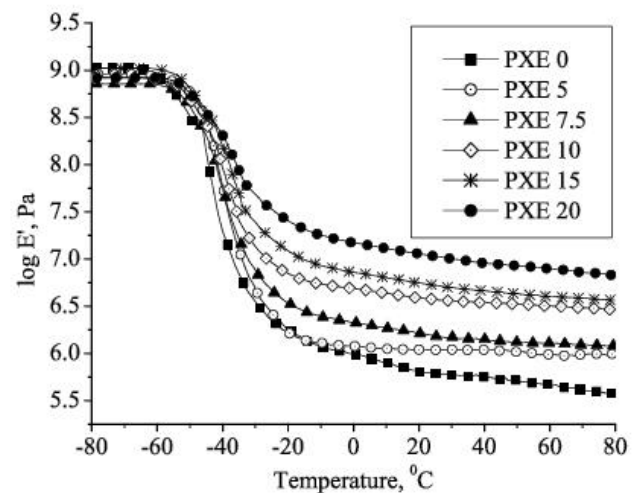


Figure 4 : Storage modulus (E') dependency on the temperature at various filler content for composites comprising Printex XE-2B carbon black

As the figures show, in the temperature interval $-80^\circ\text{C} \div -45^\circ\text{C}$ all vulcanizates studied are in the glass state regardless of the filler used. No significant changes in the values of storage modulus (E') as a function of filler amount have been observed in the said temperature interval. The storage modulus (E') values of the composites in that interval are commensurable (about $9 - 9.2$ Pa) no matter the type of the filler and its amount. At about -40°C coinciding with the transition from the glass to high elastic state the storage modulus (E') values start to decrease. There is an increase in the storage modulus (E') values with the increasing filler amount for all composites studied in the interval $-30^\circ\text{C} \div 80^\circ\text{C}$ when the composites are in the high elastic state. That

is on account of the restricted, decreased mobility of the macromolecules following their immobilization onto the fillers surface and first of all because of the immobilization onto carbon black particles. In correspondence with^[7] the effect may be used as a measure for fillers reinforcing activity, because when the filler reinforcing activity is stronger, the motion is more hampered, hence the increase in E' is also stronger.

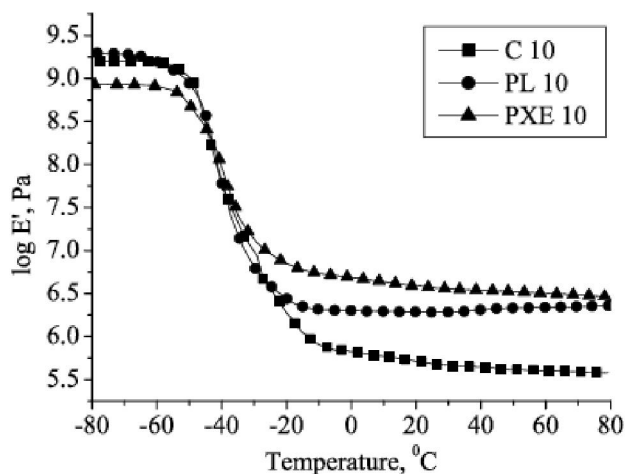


Figure 5 : Storage modulus (E') dependency on the temperature for composites comprising different type of fillers at 10 phr

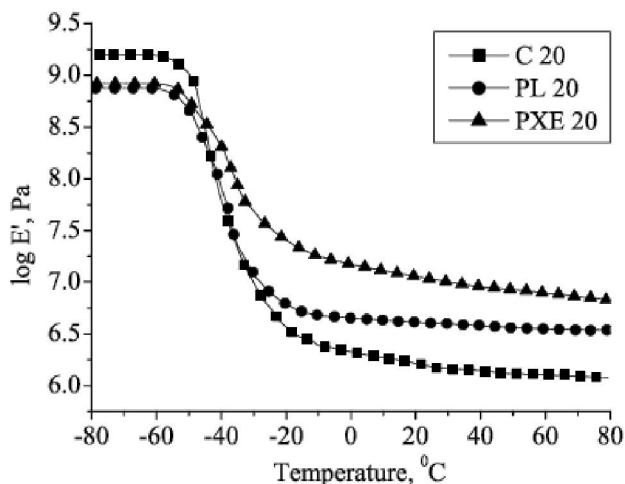


Figure 6 : Storage modulus (E') dependency on the temperature for composites comprising different type of fillers at 20 phr

Figures 5 and 6 present the temperature dependence of storage modulus (E') of the vulcanizates filled with all the fillers studied at 10 phr (Figure 5) and 20 phr (Figure 6). The figures illustrate the changes in the composites dynamic properties caused by the differences in the carbon black used.

As Figures 5 and 6 show in the interval $-30^{\circ}\text{C} \div 80^{\circ}\text{C}$ the composites studied being in the high elastic state and having the same filler amount those comprising Corax N220 possess the lowest storage modulus (E') values. In the particular temperature interval storage modulus (E') values increase in the following order: Corax N220 < Printex L6 < Printex XE-2B. The result is expected having in mind that the specific surface area determined by the filler's particle size increases in the same order. As said above the higher specific surface area of the filler particles benefits the elastomer-carbon black interaction revealed by higher storage modulus (E') values.

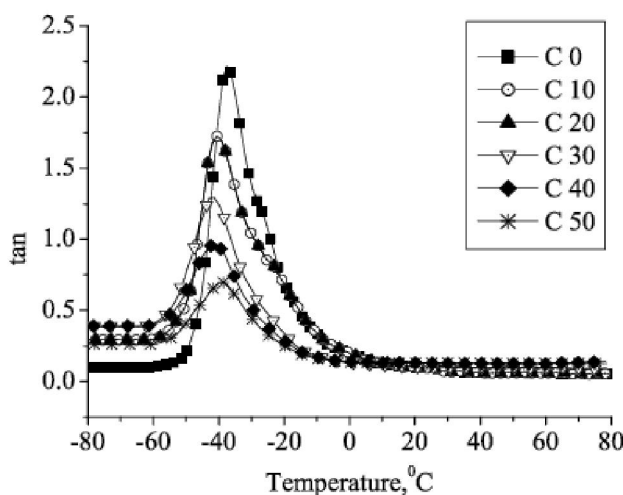


Figure 7 : Dependency of mechanical loss angle tangent ($\tan \delta$) on the temperature at various filler content for composites comprising Corax N220 carbon black

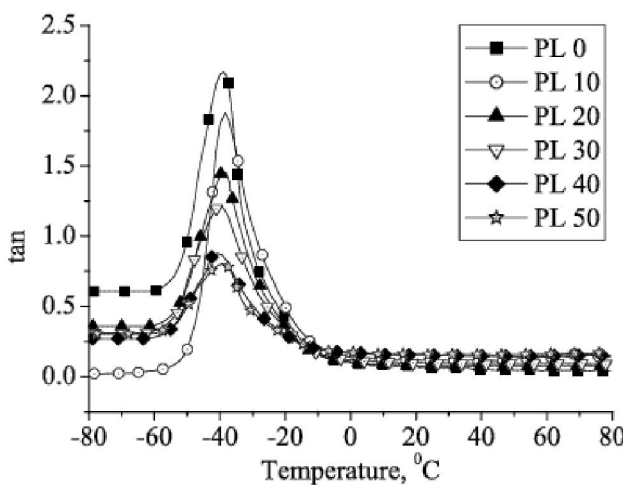


Figure 8 : Dependency of mechanical loss angle tangent ($\tan \delta$) on the temperature at various filler content for composites comprising Printex L6 carbon black

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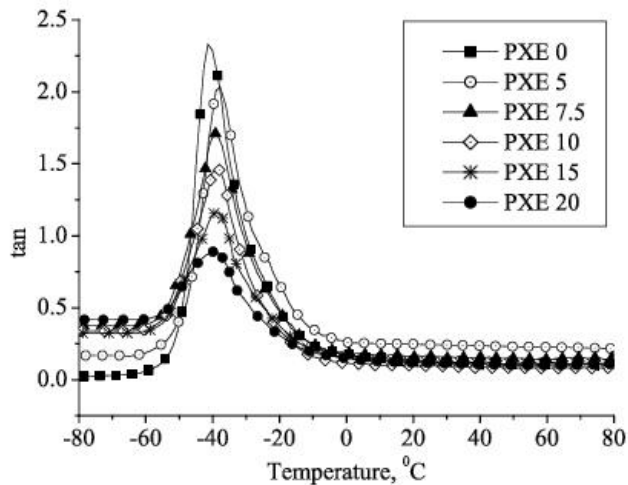


Figure 9 : Dependency of mechanical loss angle tangent ($\tan \delta$) on the temperature at various filler content for composites comprising Printex XE-2B carbon black

$\tan \delta$ being the ratio between the dynamic loss modulus (E'') and dynamic storage modulus (E') ($\tan \delta = E''/E'$) illustrates the macromolecules mobility as well as the phase transitions in the polymers^[8]. Figures 7, 8 and 9 plot the dependencies of mechanical loss angle tangent ($\tan \delta$) on the temperature at a various content of Corax N220 (Figure 7), Printex L6 (Figure 8) and Printex XE-2B (Figure 9).

As seen from Figures 7, 8 and 9 in the $0^\circ\text{C} \div 80^\circ\text{C}$ interval there are no significant differences in mechanical loss angle tangent ($\tan \delta$) dependency on the amounts of carbon black used. It is known the mechanical loss angle tangent ($\tan \delta$) peak for the composites studied to be in accordance with the glass transition temperature (T_g). In all cases studied a change in the filler amount leads to a change in T_g of about $2\text{-}3^\circ\text{C}$. Evidently, the type of carbon black has no considerable effect upon T_g of the vulcanizates investigated. It is about -40°C . Figures 7, 8 and 9 show the customary decrease of $\tan \delta$ peak intensity with the increasing amount of all three fillers that is caused by the reinforcement effect of carbon black.

Figures 10 and 11 present the temperature dependence of mechanical loss angle tangent ($\tan \delta$) for the vulcanizates comprising the three fillers studied at 10 phr (Figure 10) and 20 phr (Figure 11).

According to Figures 10 and 11 in the $0^\circ\text{C} \div 80^\circ\text{C}$ interval at there are no significant differences in mechanical loss angle tangent ($\tan \delta$) dependency on the

type of carbon black used at the same amount. The Figures reveal that the smaller the filler's particles the higher their specific surface area, hence the lesser the intensity of $\tan \delta$ peak. The effect is more pronounced at higher concentrations of the fillers used (Figure 11).

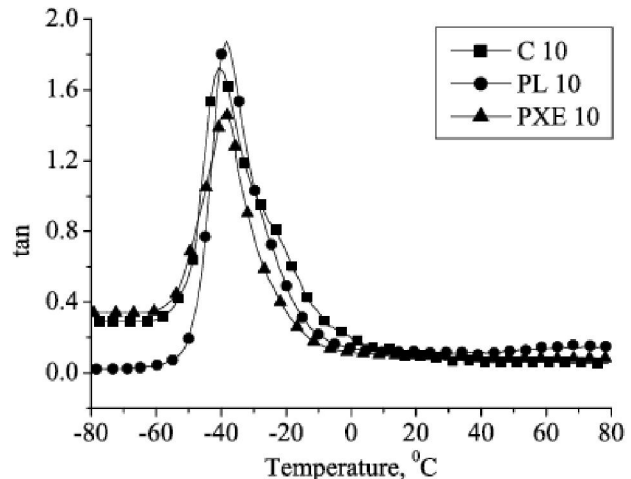


Figure 10 : Dependency of mechanical loss angle tangent ($\tan \delta$) on the temperature for composites comprising different fillers at 10 phr

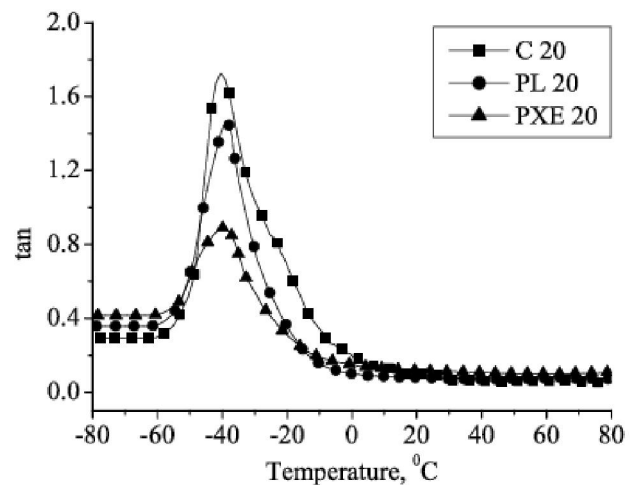


Figure 11 : Dependency of mechanical loss angle tangent ($\tan \delta$) on the temperature for composites comprising different fillers at 20 phr

The data obtained allow the conclusion that at the same concentration Printex XE-2B carbon black has a more pronounced beneficiary effect upon the mechanical properties of the natural rubber based composites if compared to that of the conventional Corax N220 carbon black.

Dielectric thermal analysis

The dielectric permittivity (ϵ') of the composites has been determined by DETA. Figures 12, 13 and 14 plot the filler amount dependence of the dielectric permittivity (ϵ') of the investigated natural rubber-based composites comprising the three types of filler whose particles size and structurality are absolutely different. The dielectric permittivity (ϵ') values have been determined at 1 KHz, 10 kHz, 100 kHz and 1 MHz, and at 30°C.

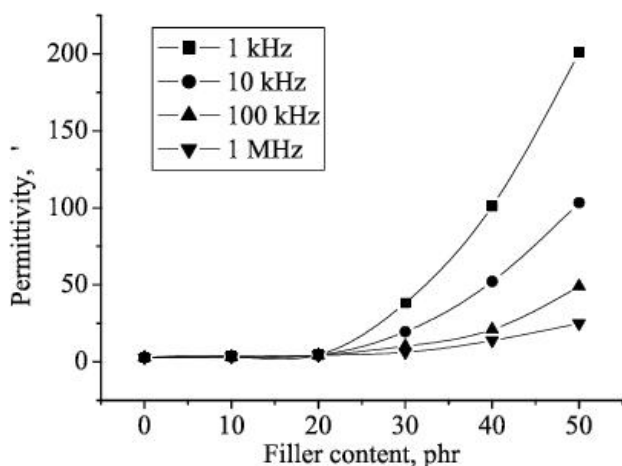


Figure 12 : Dependency of the dielectric permittivity (ϵ') at various filler content and temperature 30°C for composites comprising Corax N220 carbon black at four different frequencies

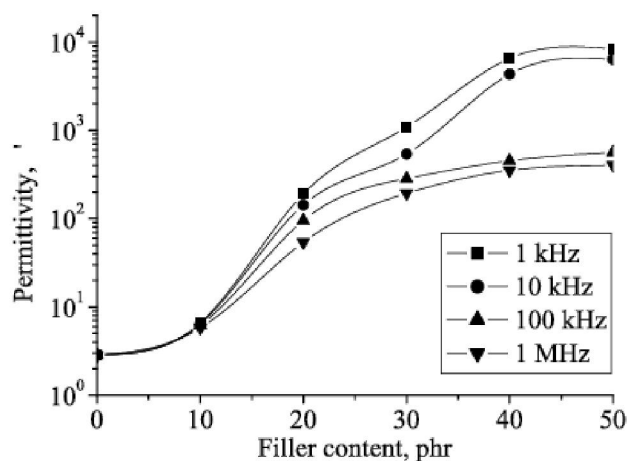


Figure 13 : Dependency of the dielectric permittivity (ϵ') at various filler content and temperature 30°C for composites comprising Printex L6 carbon black at four different frequencies

The plots in Figures 12, 13 and 14 reveal that at all studied frequencies the dielectric permittivity (ϵ') increases at a higher amount of each filler. In the case of high structure Printex XE-2B carbon black the effect is more pronounced. The change in the dielectric permittivity (ϵ')

values for composites comprising this filler occurs only at 7,5 phr. In the case of Printex L6 carbon black ϵ' values start to increase at a filler amount over 10 phr, while for Corax N220 carbon black the process is observed at about 30 phr. In all cases the frequency does not have a significant effect upon the dielectric permittivity (ϵ') since the elastomer matrix is the determining factor. At filler concentrations higher than the one mentioned for each filler the increasing frequency causes a decrease of the dielectric permittivity. As Figures 13 and 14 show the percolation threshold for composites comprising Printex XE-2B carbon black to be at about 10 phr, while for those filled Printex L6 carbon black it is at about 20 phr. According to Figure 12 the critical concentration of Corax N220 carbon black is higher than 30 phr. Such concentration facilitates the formation of electroconducting pathways which favour the polarization of the system. That means in the case of composites comprising conventional Corax N220 carbon black the percolation threshold is reached and passed at a filler amount higher than 30 phr. As seen the dielectric permittivity (ϵ') values for composites comprising maximum Corax N220 carbon black are a couple of orders lower than those of the respective composites filled with Printex XE-2B and Printex L6 carbon black. That might be explained by the lower specific surface area of the former carbon black which limits the interactions between the filler particles, hence a higher filler amount is necessary for the formation of electroconducting pathways.

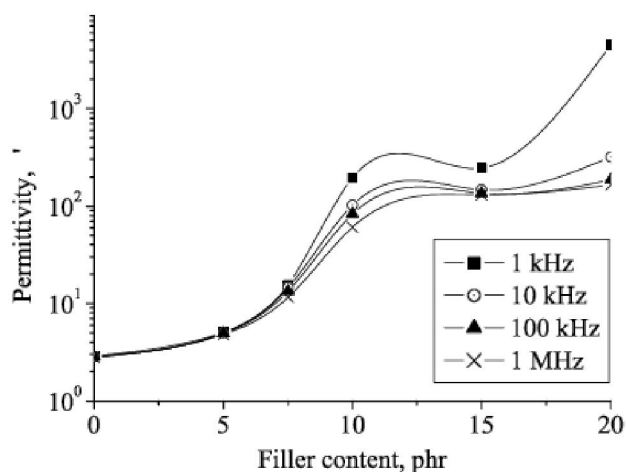


Figure 14 : Dependency of the dielectric permittivity (ϵ') at various filler content and temperature 30°C for composites comprising Printex XE-2B carbon black at four different frequencies

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Figures 15 and 16 present the frequency dependence of the dielectric permittivity (ϵ') at 30°C for the composites comprising different fillers at 10 phr (Figure 15) and 20 phr (Figure 16).

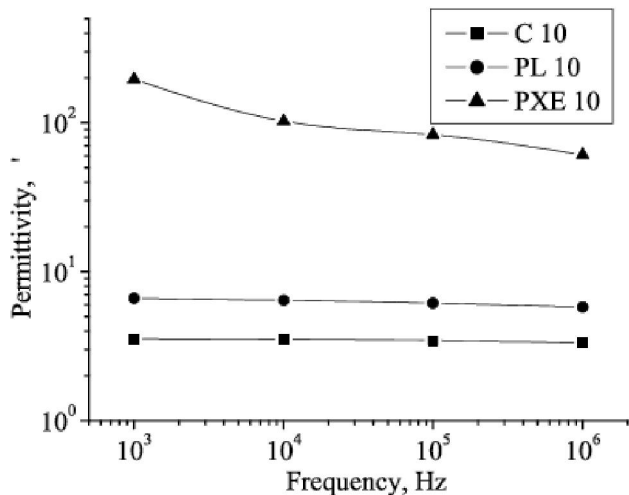


Figure 15 : Frequency dependence of the dielectric permittivity (ϵ') at 30°C for the composites comprising different fillers at 10 phr

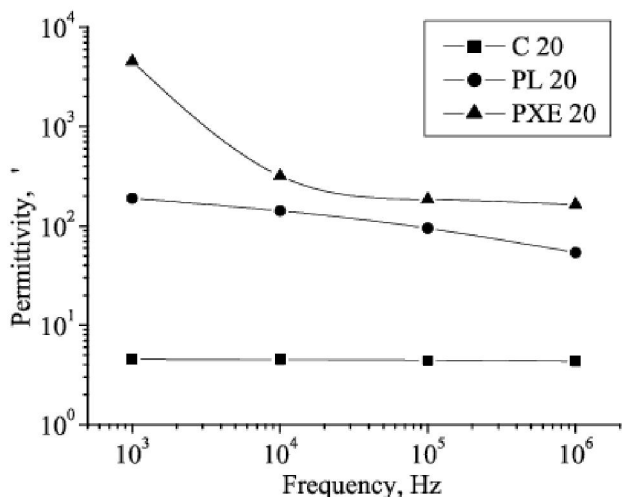


Figure 16 : Frequency dependence of the dielectric permittivity (ϵ') at 30°C for the composites comprising different fillers at 20 phr

As Figures 15 and 16 show at any of the studied frequencies the composites comprising conventional low structure carbon black Corax N220 have the lowest dielectric permittivity (ϵ') values. In those cases the elastomer matrix is the factor determining the parameter discussed. When the particle size of the carbon black studied decreases, its specific surface area increases what leads to significantly higher dielectric permittivity (ϵ') values. At the same concentrations of the fillers stud-

ied those values for the composites filled with high structure carbon black are two-three orders higher than the ones for the composites filled with Corax N220. Hence, for the those composites it is the phase of the filler that determines the dielectric permittivity (ϵ').

Figures 17 and 18 present the frequency dependence of the dielectric permittivity (ϵ') for the composites comprising different fillers at 10 phr (Figure 17) and 20 phr (Figure 18) studied at 80°C.

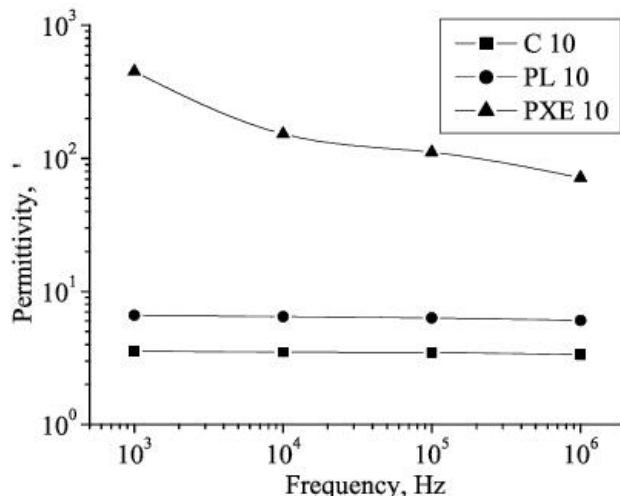


Figure 17 : Frequency dependence of the dielectric permittivity (ϵ') at 80°C for the composites comprising different fillers at 10 phr

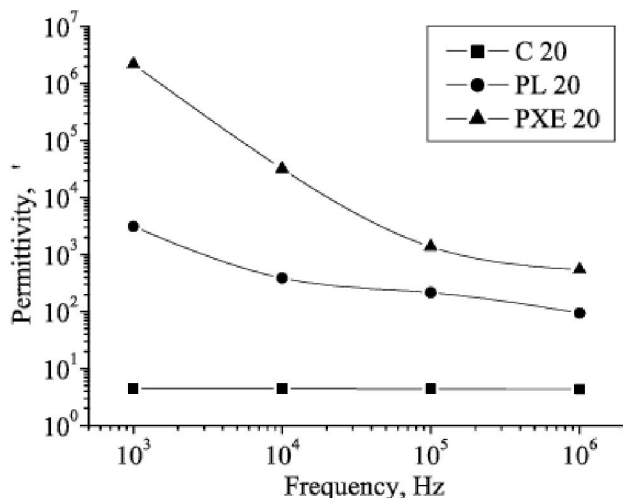


Figure 18 : Frequency dependence of the dielectric permittivity (ϵ') at 80°C for the composites comprising different fillers at 20 phr

The figures show the tendency of change in the dielectric permittivity (ϵ') values at 30 °C to be sustained at 80 °C. In all the cases the increase in tem-

perature leads to a significant increase in those values. The effect is more pronounced for the composites comprising a greater amount of carbon black and in particular for the ones comprising the high structure type Printex XE-2B.

The explanation of the effects observed under all other identical conditions (the same elastomer matrix, the same filler concentration, the same preparation of the composites and their vulcanization) could be found in the specific characteristics of each filler. As seen from TABLE 1 the values for those parameters differ completely. Hence, the factors determining the great differences in the composites properties are:

- Particle-particle interactions, aggregation and agglomeration.
- Filler particles electrical conductivity and dielectric permittivity.
- Particle surface morphology and roughness.
- Specific surface area.
- Surface free energy.

CONCLUSIONS

The effect that the specific characteristics of three completely different carbon black have upon the dynamic mechanical and dielectric properties of natural rubber based composites filled at different concentrations has been established experimentally. A comparison of the effect produced by carbon black of super high specific surface area and the one resulting from conventional carbon black has been made.

It has been found that the size of carbon black particles, its specific surface area, respectively, as well as the ability of carbon black particles to form various aggregates and agglomerates affect both the dynamic mechanical and dielectric properties of the prepared composites. At the same concentration of all fillers studied the dynamic mechanical properties of the composites filled with high structure carbon black having super high specific surface area are much better than those of the composites filled with conventional carbon black. The same is valid for their dielectric permittivity (ϵ') values which are of about two-three orders higher.

The comparative study demonstrates that the dynamic mechanical and dielectric properties of rubber composites can be tailored via an appropriate selection

of the filler which specific chemical nature and structure are capable of yielding the parameters required for the particular applications.

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