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Effects of Ceramic Fillers on the Mechanical and Thermal Transport Properties of Butyl Rubber in the Presence of Carbon Black

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Abstract

Design of experiment was conducted to study the effect of alumina micro particles as a ceramic filler alone or along with two other ceramic fillers, boehmite and silicon carbide, on curing characteristics as well as the mechanical and thermo-physical properties of carbon black filled butyl rubber-based curing tire bladder composite. The effect of using silane coupling agent, X50S as well as increasing the polarity and stiffness of the polymer matrix by replacing the butyl rubber with chlorobutyl were also investigated. Examination of rheometry curing behavior of rubber compounds showed that alumina has a slight reduction effect on curing rate and maximum torque, which improves with the presence of the modifier, X50S. Boehmite showed a reducing effect on curing rate and maximum torque while the performance of silicon carbide was similar to that alumina. Also, the hardness of the composite increased with the presence of alumina similar to that SiC and decreased with the presence of boehmite and the resilience of the composites remained unchanged in the presence of ceramic fillers. A slight decrease in the tensile strength of the carbon black-filled butyl composites was observed in the presence of ceramic fillers both individually and as a blend. However, the study of the thermo-physical properties showed that the heat transfer coefficients of the butyl composites increase in the presence of alumina in the optimal amount of its use and are similar to the effects of SiC. However, it was not possible to further increase the heat transfer coefficients by further increasing the amount of alumina even in alloy conditions with SiC and boehmite, which was attributed to the reduction of filler dispersion in the polymer matrix that validated through optical dispergrader and FESEM/MAP analysis. The use of modifier along with alumina had only a small effect on improving

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the heat conductivity of butyl rubber. Also, changing the polarity and stiffness of the rubber matrix by completely replacing the butyl rubber with chlorobutyl did not show an effect on improving the thermal conductivity of the rubber in the presence of large amounts of alumina. It was concluded that alumina micro particles have the ability to be used in bladder rubber formula along with carbon black to improve the thermal conductivity of the rubber composite only to a limited extent.

Key words

Heat conductivity, Butyl rubber, Alumina, Boehmite, Phonon scattering

1. Introduction

Butyl rubber is an elastomeric copolymer of isobutylene with small amounts of isoprene (less than 3%)[1]. The vulcanized butyl rubber shows the lowest permeability against moisture and gases among elastomers, so it has been widely used in the inner tubes of bias tires [2]. Also, the inner liners of modern radial tires are based on halogenated forms of butyl rubber (chlorobutyl and bromobutyl). Combination of impermeability with low glass transition temperature properties, flexibility and good mechanical properties, good resistance to oxidizing chemicals and silicone and vegetable oil, good heat, oxygen and ozone resistance, high damping characteristics and environmental compatibility have led to its widespread industrial use[1], which is the most important use in tire bladders [3]. These excellent properties are due to the low unsaturation of the long chains of this elastomer[4]. Except in special cases where the use of unfilled butyl rubber is addressed [5], in most industrial applications, butyl rubber needs to be compounded with suitable fillers. Various fillers such as carbon black [6, 7], white minerals [8], amorphous silica [9], alumina [10], iron oxide [11], organoclay [12, 13] and nano graphene oxide [14] have been studied in butyl rubber. The filler changes the processing, mechanical, electrical, thermal and permeability properties of rubber. Heat conductivity and thermal diffusivity are other important properties of butyl rubber that change with the arrival of the filler and in many areas of application of butyl rubber can be important. Carbon black is a classic butyl rubber filler that is able not only to reinforce and improve the mechanical and permeability properties of butyl rubber, but also to improve its heat conductivity [15]. Various heat conductive fillers also have

this potential, including metal powders, metal oxides, non-oxide carbides, graphite, graphene, nano-graphene and carbon nanotubes [16]. The thermal conductivity of an elastomeric composite is controlled by the intrinsic thermal conductivity of the filler and the rubber, the amount of filler, the size, the shape, the dispersion state and the degree of interaction of the filler with the elastomeric matrix [16]. Among these, ceramic materials are seen as a large family of fillers used in polymers, whose ability to increase the thermal conductivity of polymer and rubber along with metal and carbon-based fillers has been addressed [17-19]. Today, elastomeric ceramic composites are recognized as a new class of materials with important application potentials [16, 20, 21]. As an example, elastomer composites with ceramic materials are hopeful candidate for the uses of flexible electronics, which combines the property of low weight and the possibility of stretching the elastomer with the thermal and electronic properties of ceramics [22-25]. A review of published scientific references on ceramic-butyl rubber composite shows that with the introduction of ceramic materials into butyl rubber, in addition to changing the mechanical and dielectric properties of this rubber, the heat transfer coefficients of the resulting composite also change, which provides the potential of different applications for it in the field of electronics, wireless communications and other new advanced fields. Meng *et al.* have shown that the introduction of boron carbide ceramic (BC) in butyl rubber causes the change of current-voltage and thermal stability characteristics, and the thermal conductivity of this rubber also changes [26]. In other studies, Chameswary *et al.* reported the combined improvement of dielectric properties and thermal conductivity of butyl rubber with ceramic materials BaTiO_3 , $\text{Sr}_2\text{Ce}_2\text{Ti}_5\text{O}_{15}$, $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$, SiO_2 and TiO_2 for flexible electronic and microwave applications [27-30]. The increase of the heat transfer coefficient with ceramic fillers can create a significant improvement of potentials in other areas of application of butyl rubber, especially in the application of butyl rubber in the form of rubber bags of tire curing called bladder. In the tire curing process, the increase of the heat transfer coefficient of this part can be important to reduce production costs [3]. This issue has been studied less in scientific references [31]. Carbon black blend with ceramic fillers in butyl rubber has also been less studied [32].

Alumina as a ceramic material with a thermal conductivity of 30-42 W/mK [20] shows higher thermal conductivity than conventional carbon black used in the rubber industry. However, this

widely used industrial material has less thermal conductivity compared to modern ceramic materials such as BN with thermal conductivity of 30-1600 W/m.K, AlN with thermal conductivity of 200-320 W/mK or Si₃N₄ with thermal conductivity of 86-155 W/mK [20], but its price is also much lower, which is a determining factor in tire applications. It is also possible to increase the dispersion of this filler and its interaction with the rubber matrix by increasing its wettability [33]. Interfacial compatibility or thermal resistance of the contact surface between the rubber matrix and the filler is an important factor that affects the heat transfer properties of the resulting composite [20]. Surface modification of filler is a method that is used alternately to reduce the thermal resistance of the contact surface and minimize the phenomenon of phonon scattering as an important mechanism to reduce the thermal conductivity of polymers [17, 20]. On the other hand, alumina blending with other fillers may also cause synergistic effects. Aluminum oxide or boehmite hydroxide with the chemical formula γ -AlO(OH) is also a ceramic material that is used as a precursor for the production of alumina and its use in micro and nano sizes in elastomers as a filler has been studied [34-37]. The potential of using boehmite and alumina nanoparticles to increase the heat transfer coefficient of elastomers is also addressed [18, 19, 33], but the use of nanoscale materials for tire application purposes faces process and cost challenges for commercialization. Based on our knowledge, the properties of butyl rubber filled with carbon black used in the tire bladder in the presence of alumina and micro-size boehmite have been less studied, so in this research, the potential of using the two mentioned materials on all physical and mechanical properties and heat transfer coefficients of the of butyl rubber filled with carbon black has been studied. In addition to the above two ceramic materials, silicon carbide, SiC has been used as another ceramic filler and the study has been done in the form of an experimental design. SiC is a new ceramic filler for polymers whose potential has recently been addressed to increase the thermal conductivity of polymers and rubber individually or in blends [20, 38]. Also, the effects of alloying of ceramic fillers with each other, the effects of alumina surface modification and also the increase of the polarity of elastomer by replacing butyl rubber with chlorobutyl on all properties including heat transfer coefficients of butyl rubber have been investigated. It should be noted that as an engineering part, in addition to thermal conductivity

properties, other properties of this part that determine its life and performance in the harsh conditions of tire curing presses should be evaluated.

2. Experimental

2.1. Materials

Alpha-type alumina ($\alpha\text{-Al}_2\text{O}_3$) with 99.99% purity, 3.2 g/cm^3 particle density and $1\text{-}45\ \mu\text{m}$ particle size was prepared from a French company (Alteo). Boehmite with chemical formula $\text{AlOOH}\cdot\text{H}_2\text{O}$ with particle size less than $38\ \mu\text{m}$ and surface area $\text{BET}=251\ \text{m}^2/\text{g}$ was prepared from Azarshahr Research Center of Iran. Silicon carbide, $\alpha\text{-SiC}$ with 99.9% purity, 2.5 g/cm^3 particle density and $1\ \mu\text{m}$ particle size produced by a Japanese company was used. XRD spectras of SiC, alumina and boehmite are presented in Appendix.

Other materials, including butyl rubber (IIR, BK1675, Nizhnekamskneftekhim inc, Russia), chlorobutyl (CIIR, Nizhnekamskneftekhim inc, Russia), chloroprene (CR, Byprene, Arlanxeo, Germany), carbon black (N330, Carbon Iran Co, Iran), castor oil (FSG, Pacific Commodities, India), zinc oxide (ZnO, Sepid Oxide Shokoohieh, Iran), stearic acid (PT. Duakuda, Indonesia), phenolic resin (SP 1045, Si Group, France) and solid paraffin (Kimia Zarrin, Iran) were used as routine materials of Kavir Tire Company.

2.2. Formulation and preparation of rubber compound

Scheme 1 presents the experimental work procedure and the materials and instruments used. A standard formula of butyl rubber in the form of a blend with a small amount of chloroprene rubber filled with carbon black, castor oil, stearic acid, zinc oxide, solid paraffin and phenolic curing resin has been used as a reference formula. This formula is widely used in the manufacture of tire bladders [3, 39]. In the first part of the study and in the form of a design of experiments, the introduction of three ceramic fillers, alumina, boehmite, and SiC into the base formula without changing any of the materials in the formula was studied. In the second and third parts of this study, the increase of the amount of alumina in the formula of butyl rubber and the presence of silane modifying agent and complete replacement of butyl rubber with chlorobutyl rubber with the aim of increasing the polarity and rigidity of the polymer matrix have been studied.

Since the properties of butyl rubber composite significantly depend on the method of preparation, the order of addition of materials and the mixing time [40], in this study, all designed mixtures were prepared in two stages and under exactly the same mixing conditions. In the first stage, butyl rubber and chloroprene were mixed in the presence of carbon black, ceramic fillers, castor oil, stearic acid and solid paraffin in a 2-liter internal mixer (Banbury) according to the same instructions. After a sufficient time, zinc oxide and phenolic resin were added to the first step mixture on a two roll mill and according to the same instructions to obtain the final compound.

2.3. Determination of curing characteristics, morphology, mechanical, thermal and aging properties of rubber compounds

Rheometry characteristics of uncured compounds were determined by an oscillating die rheometer (ODR 2000 E, Alpha technologies) at 185 °C for 30 min. These characteristics include minimum torque (ML), maximum torque (MH), scorch time (t_{s2}), optimum curing time (t_{90}) and curing rate. To determine the tensile properties and tearing force, rubber plates with a thickness of about 1-2 mm were prepared in a suitable mold in the curing press at 185 °C for 50 min and then punched. Punched dumbbell (Tensile) and Die C (Tear) specimens were tested in a tensile test machine (5–10 K-S, Hounsfield, UK). Tensile strength, elongation at break (EAB), modulus 200 (M200) and tear strength have been reported. Also, to determine the aging coefficient, the tensile test was performed on dumbbell-shaped samples that were aged in an oven for 72 h at 100 °C. To calculate the aging coefficient (A), the product of tensile strength and elongation at break after aging is divided by the product of tensile strength and elongation at break before aging. Hardness and resilience tests were performed on butyl and chlorobutyl cured samples (at 185 °C for 50 min) according to the standard by Shore A durometer (Zwick 3100, Germany) and resilience meter (Wallace UK Dunlop Tripsometer R2). Filler dispersion index in rubber matrix was determined by Dispergrader 1000 (OptiGRADE, Sweden), an optical microscope. To determine this index, the prepared material is compared with the reference and is ranked from 1 to 10 by computer. The specific heat capacity of the cured samples was determined by differential scanning calorimetry (DSC) (METTLER STARe SW12) according to ASTM E1269-1. The density of the cured samples was determined by immersion in water and Archimedes

relationship. Finally, SEM imaging and EDX spectrum recording by MIRA3 FE-SEM/ EDX (Tescan, Czech Republic) has been performed to characterize the dispersion state of each filler.

2.4. Determination of conductivity and thermal diffusivity coefficients of rubber composites

An experimental/numerical/guess and error hybrid approach was used to calculate the thermal diffusion coefficient and thermal conductivity (k) of butyl rubber compounds, which was first reported by Ghoreyshi *et al.* [41] and was further simplified [18, 19]. First, a rectangular sample of rubber with dimension of $5 \times 5 \times 2$ cm³ with a thermocouple wire in the center was made at a temperature of 185°C for 50 min with the help of a suitable mold. The samples were then immersed in an oil bath for 30 min and the temperature changes of the center point of the sample over time were recorded using a temperature recorder. In the present study, in order to ensure more reliability in determining the value of k at temperatures close to the bladder performance in tire curing process, immersion test was performed for each sample at three different temperatures of oil bath (140, 150 and 160 °C). Then, in the next step, with the help of simulation of the above geometry in ABAQUS software, thermal diffusivity was calculated by guess and error. In order to simulate, the problem geometry was defined in the software and then the time-dependent 3D heat transfer equation (Eq. 1) was solved in Cartesian coordinates by determining the appropriate boundary situation. ρ , k , and C_p in Eq. 1 are density, heat conductivity, and specific heat capacity, respectively. Assuming the values of ρ , k , and C_p are constant, Eq. 1 converts to Eq. 2. It should be noted that α in Eq. 2 is the coefficient of thermal diffusion, α , which is related to the specific heat capacity, density and heat conductivity of the rubber sample according to Eq. 3.

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(k \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) \quad (1)$$

$$\frac{1}{\alpha} \frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \quad (2)$$

$$k = \alpha \rho C_p \quad (3)$$

To simplify calculations, thermal coefficients were considered to be constant and independent of temperature and the values in different temperatures of oil bath was measured and averaged.

The process was in a way that the value of thermal diffusion coefficient was selected as guess and error in order that the predicted value of temperature changes in the sample center would match the experimental value available. Meanwhile, considering that the heat transfer coefficient of oil, \bar{h} is dependent on temperature, this coefficient has been calculated separately in three test temperatures (140, 150, 160 °C). To calculate \bar{h} , the following formula was used, which has been presented for an immersed body in a fluid [42].

$$\bar{h} = 0.52 \frac{k}{l} (Ra_l)^{\frac{1}{4}} \quad (4)$$

$$Ra_l = GrPr = \frac{g\beta(T_s - T_\infty)L^3}{\nu\alpha} \quad (5)$$

\bar{h} in the above equation is convective heat transfer coefficient and Ra is Rayleigh number, which is the product of Grashof number (Gr) and Prandtl number (Pr). The coefficients k , ν and α are the thermal conductivity coefficient, kinematic viscosity and thermal diffusivity coefficient of the used oil, respectively, which were determined from the relevant reference tables at three test temperatures [42]. β is also the thermal expansion coefficient. Thus, the value of \bar{h} at three temperatures of 140, 160 and 180 °C was calculated to be 183, 210.7 and 255.9 W/m².K, respectively and was used in the simulation process in each of the three oil bath temperatures. To calculate the thermal conductivity of composites, heat capacity data are needed that has been determined by the DSC test. The obtained values of heat capacity (C_p), which is dependent on temperature, were averaged in the range of ambient temperature to oil bath temperature and were used to determine the coefficient of thermal conductivity of composites (k) according to the Eq. 3. α of rubber composite obtained by simulating the experimental temperature-time-point data at the center of each sample. Also, in each simulation process for a specific sample, 3 to 4 values for α were calculated due to the fact that in the simulation process, different values of α in a limited range were able to produce a simulation curve in accordance with the experimental data. Due to the fact that the immersion test in the oil bath was performed for two rubber pieces for each formula and for each piece, four values of α are calculated and this is done in three different oil bath temperatures, the average value reported for α and k is the average of 24 data for each formula. However, this process has been performed only for the 8 formulas studied in the form of an experimental design, and for studies of the modifying effect and

increasing the polarity of the butyl matrix, only two samples have been performed at one temperature. Therefore, the results reported in the second part of this study are an average of 8 data (two samples at one temperature).

3. Results and Discussion

In the first series of formulas of this research, the effect of carbon black (CB) blending with three heat conductive ceramic fillers including alumina, boehmite and SiC on all mechanical and thermo-physical properties of the butyl based composites has been studied. The design of experiments has been used to study the main effects of these three ceramic fillers.

In the second series of this study, the increase of the amount of alumina and also the effect of alumina surface modification using a silane coupling agent (X50S) has been studied and in the third part, complete replacement of the butyl polymer matrix with chlorobutyl in the presence of alumina and boehmite has been investigated. The levels of formulation variables are given in Tables 1 and 2 next to the properties studied. Formulations 1 to 8 are for the first series (test design), formulas 9 to 12 are for the second part (modification effect), and formulas 13 to 17 are for the third series (chlorobutyl rubber effect). The rheometric results of the compounds are shown in Table 1. Also, mechanical properties, dispersion index, aging index and coefficients of thermal diffusivity and heat conductivity for rubber composites are listed in Table 2. For the results of the first part, the main effect curves have been drawn to study the average behaviors of ceramic fillers. In the formulas presented in the first series, which are based on the experimental design, binary filler system, CB/alumina, CB/boehmite, CB/SiC, ternary filler system, CB/alumina/boehmite, CB/alumina/SiC, CB/SiC/boehmite and quaternary filler system CB/alumina/boehmite/SiC has been studied. The main effect curves for rheometric properties have been shown in Figure 1. Figure 1 (a), 1 (b), 1 (c) and 1 (d) are the main effects of alumina, SiC and boehmite on the properties of minimum torque, maximum torque, optimum curing time and rheometric curing rate of butyl rubber, respectively. Except for boehmite, which shows a significant reduction effect on maximum torque and curing rate and an increasing effect on curing time, in other cases, the addition of ceramic materials to butyl rubber shows little effect on rheometric properties. Butyl rubber is vulcanized with various curing agents, such as sulfur,

quinone, and resin [43]. Resin curing is preferred for products that are exposed to high temperature fluids such as bladder [39]. Resin curing (phenol-formaldehyde) is activated with halogen-containing compounds (such as chloroprene rubber) along with zinc oxide [39]. However, the curing rate of butyl rubber resin is low and it is done at high temperature and for a long time. The rheometric results of Table 1 show the values of low curing rate and long curing times for butyl rubber formulas in the presence of CB and CB/ceramics. Among ceramic fillers, boehmite-containing mixtures show a sharp decrease in rheometric properties, indicating that boehmite interferes with the butyl rubber resin curing process. However, alumina similar to SiC makes slight changes in the curing rate, curing time and torque of butyl rubber filled with carbon black.

The effect of ceramic fillers on all mechanical, thermo-physical and aging properties of CB-filled butyl rubber has been shown in figures 2 and 3. Figures 2a, 2b, 2c, and 2d are related to tensile strength, tear strength, modulus 200%, and elongation at break of CB-filled butyl rubber in the presence of three ceramic fillers, respectively. One exception for increasing the tear strength and elongation is observed in boehmite, but in general, the presence of ceramic fillers shows a significant slight decrease in tensile strength, tear strength, modulus and elongation of butyl rubber compared to the reference state. The tensile strength values of butyl rubber compounds in bladder formula are low compared to filled natural rubber and styrene butadiene rubber. The tensile strength of the CB reference composite without ceramic filler (No. 1) is about 11 MPa, which is close to the values of tensile strength reported in other references with the same formula [3]. Tensile strength does not change much in the presence of 10 Phr of alumina or 20 Phr of SiC (slight decrease) but in the presence of boehmite and also when the total amount of ceramic material in the rubber increases (30 and 40 Phr), a greater decrease in tensile strength is observed. It can be reduced to less than 10 MPa, so in terms of strength properties, increasing the amount of ceramic filler in CB-filled butyl rubber is limited.

Figure 3 shows that the density and hardness of mixtures increase with the presence of ceramic fillers, which is due to the hydrodynamic effect of the presence of a hard filler in the rubber composite. The resilience of CB-filled butyl rubber remains unchanged in alloying with ceramic fillers (Figure 3b). The same conditions exist for aging coefficient and the changes in the entry of

ceramic filler on this coefficient are not very significant. Thermal stability and aging resistance of butyl rubber resin curing are inherently high due to C-C bonds in the rubber [43]. This is determined by the high values of the aging coefficient presented in Table 2. Similar small changes for the tensile properties (tensile strength and elongation) of butyl rubber with the same formula under aging conditions have been reported in other references[3, 43]. However, an increase in the stability strength of butyl rubber by a boron carbide ceramic filler has also been reported by Meng *et al.* [26]. They have stated that ceramic fillers have high thermal stability, which have the ability to absorb the heat entering the composite and delays the thermal degradation of the polymer.

Figure 4 shows that the ceramic fillers have a clear decreasing effect on the filler dispersion index in the butyl rubber substrate. According to Table 2, the filler dispersion index in butyl rubber filled with carbon black is 8. But with the advent of ceramic fillers, the dispersion index drops to less than 5. The decrease in elongation and tensile strength of butyl rubber in the presence of ceramic fillers is may be due to dilution effect (the reduction of the rubber part in the formula) as well as the reduction of the filler dispersion and rubber-filler interaction. The increase in the elongation of butyl rubber in the presence of boehmite is due to the decrease in crosslink density.

Finally, Figure 5 shows the average effects of ceramic fillers on the heat conductivity and thermal diffusivity of the butyl rubber composites in the presence of carbon black. Alumina performs better than boehmite but it is weaker than SiC in heat conduction characteristics. In this study, it is assumed that the thermal diffusion coefficients of butyl rubber are independent of temperature. Gwaily *et al.* showed that the thermal diffusion coefficient of butyl rubber filled with 50 Phr carbon black in the presence of small amounts of BaTiO₃ ceramic is almost constant and independent of temperature [31]. Bafnec *et al.* showed that the thermal diffusion coefficient of CB-filled rubber decreased with temperature with a slight slope, but the changes were especially small at high temperatures [44]. In the present study, this coefficient is considered independent of temperature and by considering an average value for heat capacity in the range of ambient temperature to oil bath temperature, the coefficient of thermal conductivity is also calculated independent of temperature. In addition, the choice of three temperatures of 140, 160 and 180 °C oil bath to determine the coefficients of conductivity and

thermal diffusivity is due to the fact that the conditions for measuring heat transfer coefficients are close to the temperature conditions experienced by Bladder in the tire curing process. The values obtained in this study for heat transfer coefficient are in the range of values reported by other researchers [44-47]. The results of this study show that CB/ceramic hybrid fillers increase the thermal conductivity and thermal diffusivity of butyl rubber compared to when only CB is used as filler. The decreasing effect of boehmite on the heat transfer coefficient is due to the fact that the average values of the coefficients from Table 2 are presented in the form of main effects and the boehmite performance in alloy with other ceramic fillers is poor, probably due to its poor dispersion as further demonstrated by FESEM. But boehmite alone shows a relative increase in the thermal conductivity (comparison of mixes 1 and 2 in Table 2).

Ceramic fillers show a reducing effect on the heat capacity of CB filled rubber composite. Temperature-dependent changes in the heat capacity of butyl rubber filled with CB (sample 1), CB/SiC (sample 3) and CB/alumina (sample 5) have been shown in Figure 6, which have been determined by the DSC test. The heat capacity of CB-filled butyl rubber is reduced in the presence of both SiC and alumina fillers.

Another important result is that the analysis of the data on heat transfer coefficients in Table 2 shows that the alloying (blending) of ceramic fillers in a way that leads to increasing the total amount of ceramic filler in butyl rubber does not result in a greater increase in heat transfer coefficients than when only a ceramic filler is used along with CB. Composite No. 6 contains 10 Phr alumina and 10 Phr boehmite (20 Phr total ceramic filler), which has a thermal conductivity of composite No. 2 containing 10 Phr boehmite and composite 5 containing 10 Phr alumina. In other words, the alloying of two different fillers (alumina and boehmite) does not help further increase of heat conductivity coefficient.

The dispersion mode of the filler in the polymer matrix is a challenging issue with the aim of optimizing the heat transfer coefficient of the composite. On the one hand, the presence of filler agglomerates in the rubber matrix and more contact of the fillers leads to the formation of heat transfer paths or conductive network structures [26]. For example, the presence of silica and alumina ceramics along with carbon black in emulsion styrene butadiene rubber has been shown to improve the heat transfer coefficient of the resulting composite due to the greater tendency

of these particles to agglomeration and the formation of paths of the heat transfer [18, 19]. On the other hand, it is stated that better filler dispersion increases the contact surface and the thermal conductivity of rubber composite [47]. Poor filler dispersion, due to less polymer-filler interaction, is also expected to create a heat transfer resistance at the interface of the filler-rubber particles, which intensifies phonon scattering in solids [16]. So it seems that there is an optimal value for ceramic filler in butyl rubber in which the heat transfer coefficient is maximized. It should be noted that this increase in thermal conductivity which was obtained in the present study with CB/ceramic fillers is a maximum of 0.36 W/m.K, which is more than the thermal conductivity of unfilled butyl rubber, which was reported in the references as 0.09-0.13 W/mK [26, 29]. Values in the same range for thermal conductivity of butyl rubber filled with BaTiO₃ micro particles (0.31 W/m.K) and BaTiO₃ nanoparticles (0.36 W/m.K) have been reported by Chameswary and Sebastian [29]. However, high values of thermal conductivity of 1.71 W/m.K for butyl rubber in the presence of large amounts (50% by volume) of BN ceramic material and higher values in the range of 1.5 to 4.5 W/m K in the presence of very large amounts of 50 to 400 Phr of Strontium Cerium Titanate ceramic material have also been reported [26, 27], although the focus of the mentioned articles is on the electrical properties and non-bladder applications of the composite, and the expected properties of these composites in the absence of carbon black can be studied separately as a research topic.

Effects of silane coupling agent and chlorobutyl rubber

Based on the results of the second series presented in Tables 1 and 2, it is determined that in a small amount of alumina (8 Phr), a slight improvement in all properties including heat transfer coefficients occurs using silane coupling agent (X50S). Although X50S modifier has an effect on improving the mechanical properties of butyl rubber filled with CB and 17 Phr of alumina (slight increase in tensile strength, modulus, tear strength and stiffness), it cannot improve the heat transfer coefficients of the composite. The comparison between the results of composite No. 1 and No. 11 shows that the heat transfer coefficients of butyl rubber does not change with the presence of 17 Phr of alumina. Also, the coefficient of thermal conductivity of mixture No. 12 (17 Phr of alumina and 1.7 Phr of silane) shows that the presence of silane coupling agent does not

cause any change in the above coefficient. The mechanism of alumina surface modification with silane modifying agent, as well as the improving effects of silane modifying on different properties of alumina-filled rubber mixtures have been addressed in a number of references for EPDM, NR and SBR/BR rubbers [19, 33]. It seems that in low amounts of alumina, the presence of silane modifying agent can also improve the various properties of butyl rubber, but in higher amounts of this filler, silane modifier is less effective in improving the heat transfer coefficients of butyl rubber.

The results of the third series of studied formulas in the last part of Tables 1 and 2 show that the curing rate and the maximum torque of rubber compounds have been increased significantly in the presence of chlorobutyl rubber compared to butyl rubber due to the presence of molecules of Chlorine and its activating effect in the resin curing system. This increase shows its effect in increasing the hardness and modulus of the resulting composite compared to the butyl composite (Table 2). Also, the results of Table 2 show that this substitution reduces the aging coefficient of chlorobutyl composites. However, the results of the third series in Tables 2 indicate that the complete replacement of butyl rubber with chlorobutyl does not have a significant change in the heat transfer coefficient of the rubber composite in the presence of CB, CB/alumina, CB/boehmite and CB/alumina/boehmite and CB/Alumina/Boehmite/SiC. This replacement increases the polarity of the rubber matrix, which is expected to affect the rubber-ceramic compatibility, but this change did not significantly affect the heat transfer coefficients. In order to summarize the effect of ceramic filler on heat transfer coefficients of butyl rubber and chlorobutyl rubber, the changes of thermal conductivity and thermal diffusivity coefficient in terms of the total amount of ceramic filler in butyl rubber and chlorobutyl rubber have been shown in Figures 7 and 8. The nonlinear dependence of the heat transfer coefficients on the total amount of ceramic filler has been shown well, which is quite clear for the thermal conductivity.

Figures 9 shows the SEM/MAP images of filler dispersion in rubber matrix. The EDS spectrum of the samples has been shown in the same figure. Fig. 9 corresponds to composite No. 8 containing alumina (10 Phr), Boehmite (10 Phr) and SiC (20 Phr). The dispersion of SiC particles is better than alumina and boehmite. As it can be seen from the pictures (Fig. 9), agglomerates are formed in

the presence of large amounts of alumina filler (alumina and boehmite) which can be effective in intensifying the phonon scattering, which is the most important factor in reducing the thermal conductivity of filled polymers. Other components of the formula, including SiC and zinc oxide, have a good dispersion. Also, the sulfur observed in both mixtures is related to the sulfur in the carbon black used, which remains in the carbon black during the process. It can be seen that sulfur also has a good dispersion, which is synonymous with a good dispersion of CB. In other words, the mixing conditions were such that all components of the formula had a good dispersion, but the tendency of alumina particles to agglomeration is the main obstacle to further increase in alumina in the formula with the aim of further increase of the heat transfer coefficients of butyl rubber.

4. Conclusion

In this study, the effect of ceramic fillers on different properties of butyl rubber in a common formula used in the tire curing bladder was studied. It has been shown that ceramic fillers increase the thermal diffusivity and thermal conductivity of composites. Among the three fillers studied, SiC and alumina performed better than boehmite. However, the use of alloys of these three fillers did not show a significant effect on the thermal conductivity of the mixtures. Also, the use of silane modifiers in small amounts of alumina caused a slight improvement in heat transfer coefficients. The mechanical and rheometric properties of carbon black-filled butyl rubber with the presence of ceramic fillers did not show a significant decrease. Therefore, it seems that the CB / alumina alloy alone or along with SiC can be used as a hybrid filler in the butyl rubber matrix for the bladder formula.

Acknowledgments

The authors of this article gratefully thank for the support of the Kavir Tire Company.

Table 1: Formulations (Phr) and cure properties of the rubber compounds

		IIR/CR	CIIR/CR	Alumina (Al/X50S)	SiC	Boehmite (BH)	ML (lb-in)	MH (lb-in)	t ₅₂ (s)	t ₉₀ (min)	RATE (lb- in/min)
Seri1: DOE	1	95/5	0	0/0	0	0	8.54	24.84	223	23.2	1.3
	2	95/5	0	0/0	00	10	8.74	22.38	300	24.6	0.9
	3	95/5	0	0/0	20	0	8.61	27.07	208	23.3	1.4
	4	95/5	0	0/0	20	10	8.58	22.38	305	25.1	0.9
	5	95/5	0	10/0	0	0	9.02	26.5	232	23.5	1.3
	6	95/5	0	10/0	0	10	8.54	22.23	312	25.1	1
	7	95/5	0	10/0	20	0	8.03	24.78	228	24.1	1.3
	8	95/5	0	10/0	20	10	8.12	21.32	324	25.3	0.9
Seri2: Silane Modification	9	95/5	0	8/0	0	0	7.40	22.90	180	21.4	1.3
	10	95/5	0	8/0.8	0	0	7.41	22.58	182	22.2	1.2
	11	95/5	0	17/0	0	0	7.06	22.46	182	22.2	1.2
	12	95/5	0	17/1.7	0	0	7.12	21.79	191	22.5	1.8
Seri3: CIIR Effects	13	0	95/5	0/0	0	0	8.19	36.07	54.00	5.16	18.70
	14	0	95/5	0/0	0	10	7.24	38.07	77.00	7.26	11.90
	15	0	95/5	20/0	0	0	6.52	33.84	61.00	4.50	17.70
	16	0	95/5	20/0	0	10	6.74	36.19	76	5.07	11.7
	17	0	95/5	20/0	10	10	6.17	33.79	72	4.55	10

Table 2: Mechanical and thermo-physical properties, aging and dispersion index of the rubber composites

	Al (Phr)	SiC (Phr)	BH (phr)	Tensile (Mpa)	Tear (kN/m)	EAB	M200 (MPa)	Hardness (Shore A)	Resilience (%)	Density (g/cm ³)	A	Dispersion	K (W/m.K)	alpha ^{10⁷} (m ² /s)	
Seri1: DOE	1	0.00	0.00	0.00	11.1	37.8	560	4.3	57	5.2	1.128	0.97	8.00	0.30	1.17
	2	0.00	0.00	10.00	10	36.1	561	3.5	58	5.2	1.159	1.00	4.00	0.33	1.31
	3	0.00	20.00	0.00	10.8	35.1	467	4.8	63	6.3	1.201	0.99	5.00	0.36	1.67
	4	0.00	20.00	10.00	9.3	40.3	543	3.6	62	5.2	1.226	0.96	3.00	0.34	1.76
	5	10.00	0.00	0.00	10.9	34.5	469	5.1	63	5.2	1.17	0.94	6.00	0.33	1.42
	6	10.00	0.00	10.00	9.2	38.7	548	3.7	65	5.2	1.198	0.97	3.00	0.33	1.42
	7	10.00	20.00	0.00	8.7	37	503	3.8	65	5.2	1.235	1.00	4.00	0.36	1.88
	8	10.00	20.00	10.00	8	33.2	507	3.2	64	5.2	1.265	1.00	3.00	0.31	1.69
Seri2:Silane Modification	9	8.00	0.00	0.00	10.3	35.1	491	4.6	67	6.3	1.160	1.00	6.00	0.37	1.59
	10	8/0.8	0.00	0.00	11.2	37.5	496	4.62	69	5.4	1.166	0.89	6.00	0.39	1.66
	11	17.00	0.00	0.00	10.8	30.1	479.5	4.22	68	5.4	1.197	0.90	3.00	0.28	1.29
	12	17.00	0.00	0.00	11.4	37	486.1	5	70	6.3	1.203	0.82	3.00	0.28	1.30
Seri3: CIIR Effects	13	0.00	0.00	0.00	10.4	21.2	232.7	9.7	76	5.2	1.133	0.71	8.00	0.30	1.19
	14	0.00	0.00	10.00	11	21.5	260	9.7	74	6.3	1.164	0.78	4.00	0.31	1.27
	15	20.00	0.00	0.00	9.5	22.8	223.1	8.7	77	5.2	1.214	0.85	3.00	0.30	1.46
	16	20.00	0.00	10.00	10	23.9	225.5	9	75	6.3	1.247	0.75	3.00	0.33	1.63
	17	20	10	10	9.0	22.6	238.8	7.7	76	6.3	1.272	0.80	3.00	0.3	1.59

Materials



Mixing



Curing



Tests



Scheme 1. The experimental work; materials and instruments for mixing, curing and tests

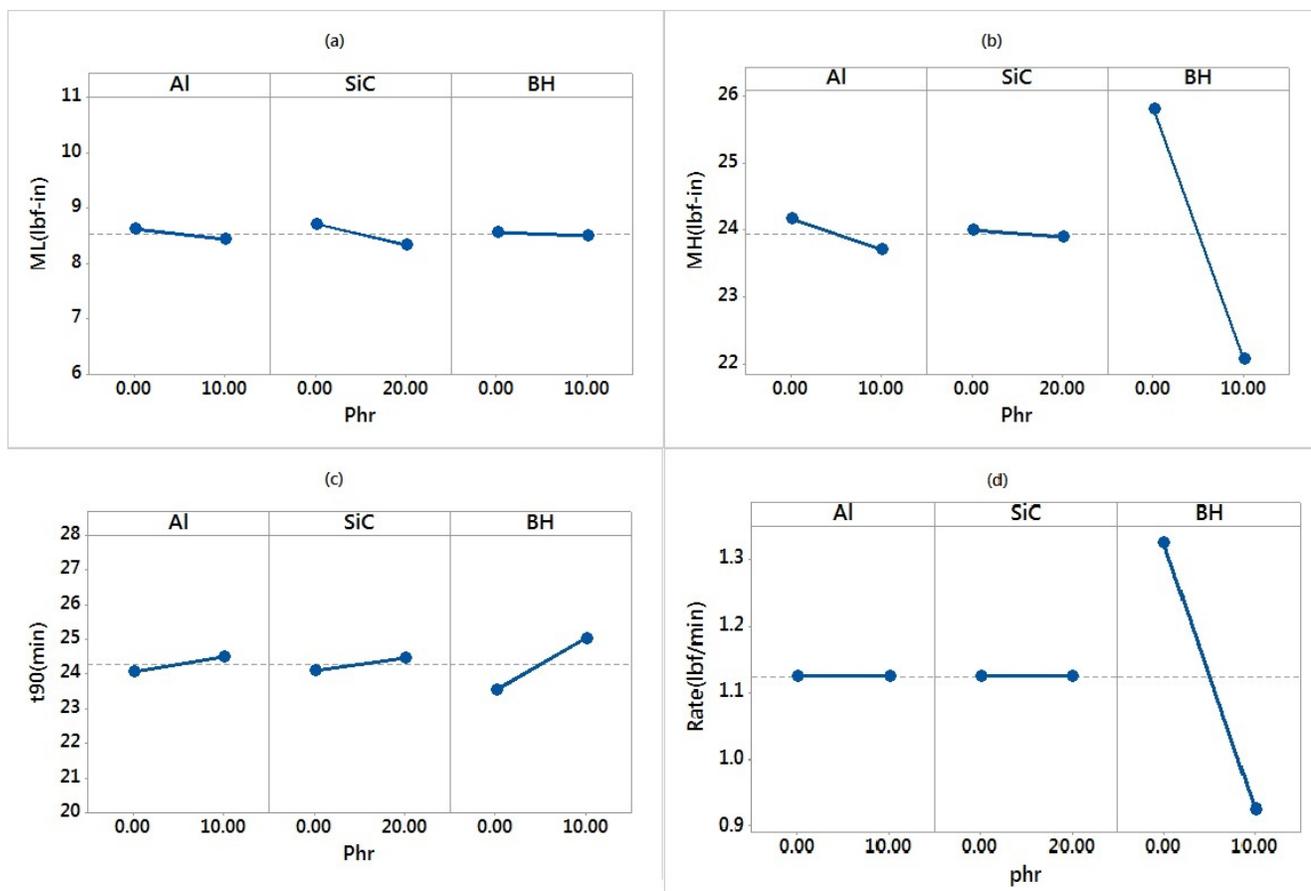


Fig. 1: The main effects plot of ceramic fillers on the cure properties of CB-filled butyl rubber

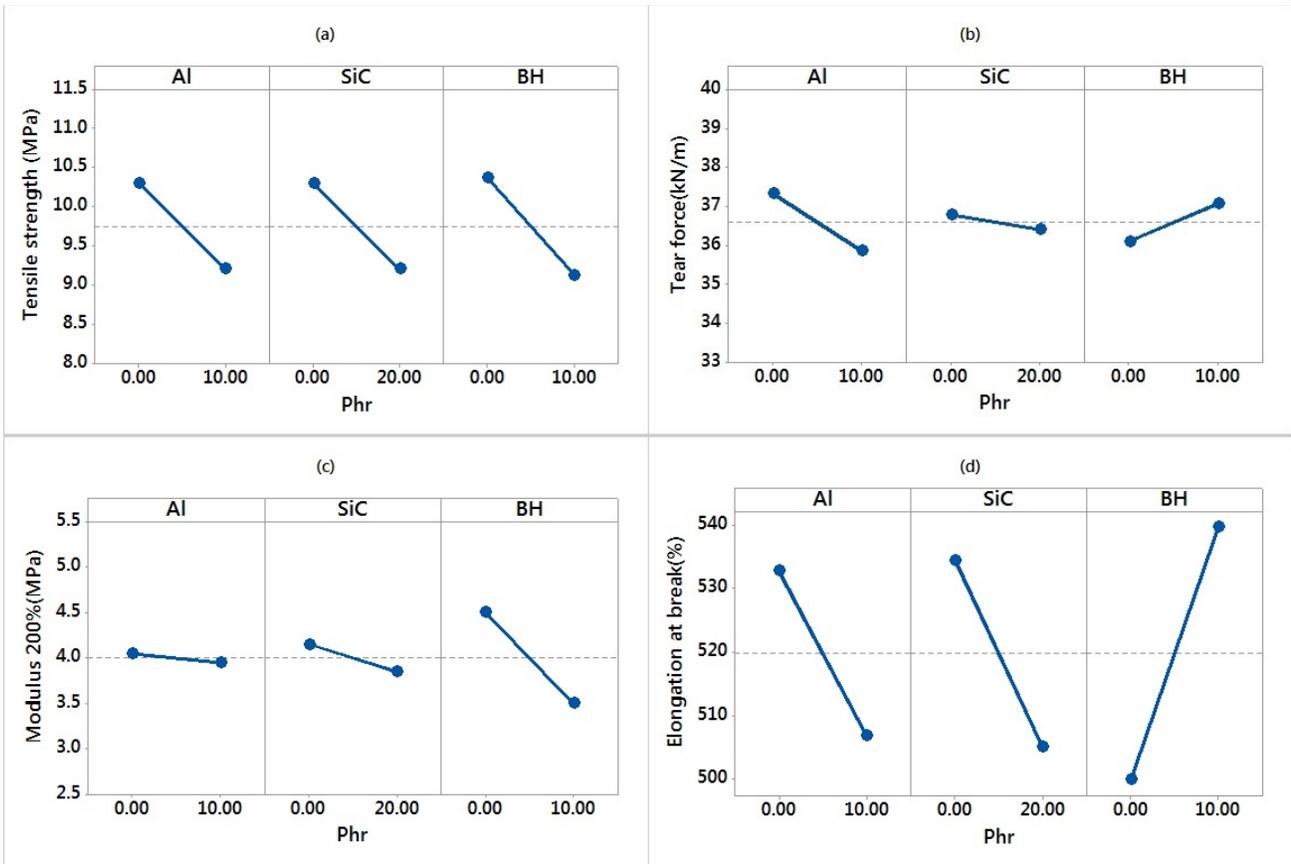


Fig. 2: The main effects plot of ceramic fillers on the properties of tensile strength, tear force, modulus 200% and elongation at break of CB-filled butyl rubber

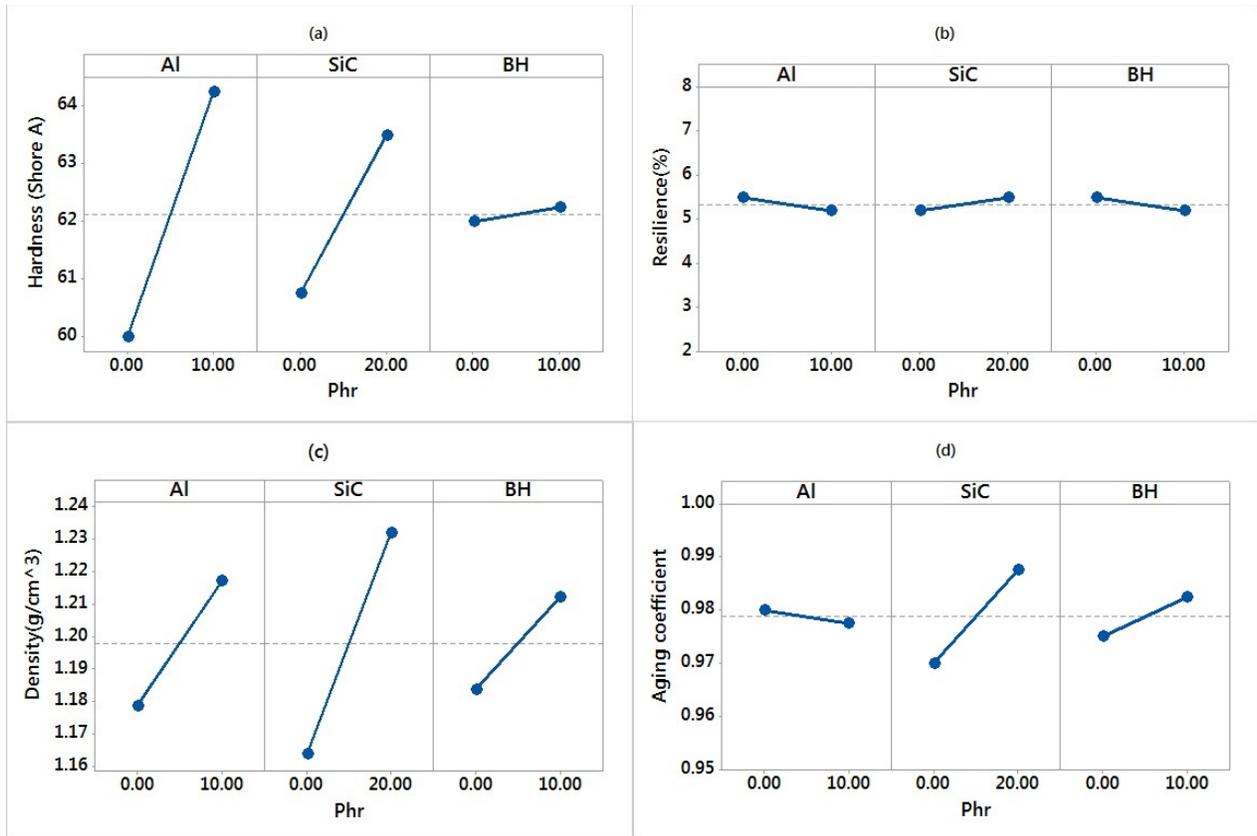


Fig. 3: The main effects plot of ceramic fillers on the properties of hardness, resilience, density and aging coefficient of CB-filled butyl rubber

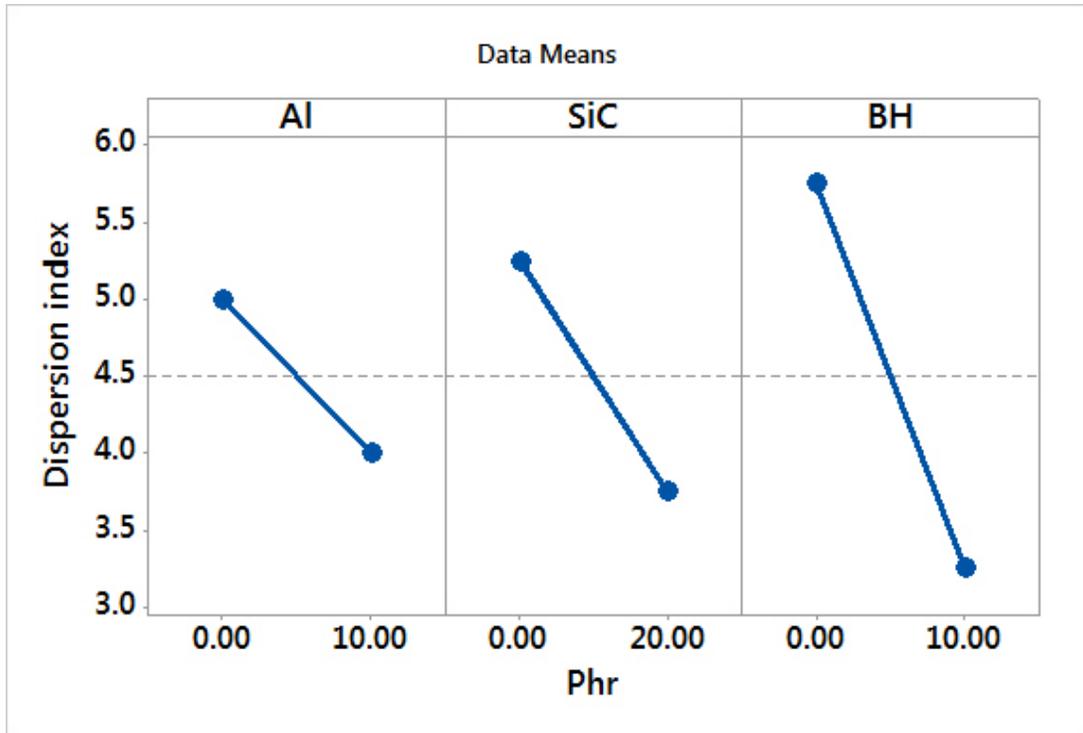


Fig. 4: The main effects plot of ceramic fillers on dispersion index of CB-filled butyl rubber

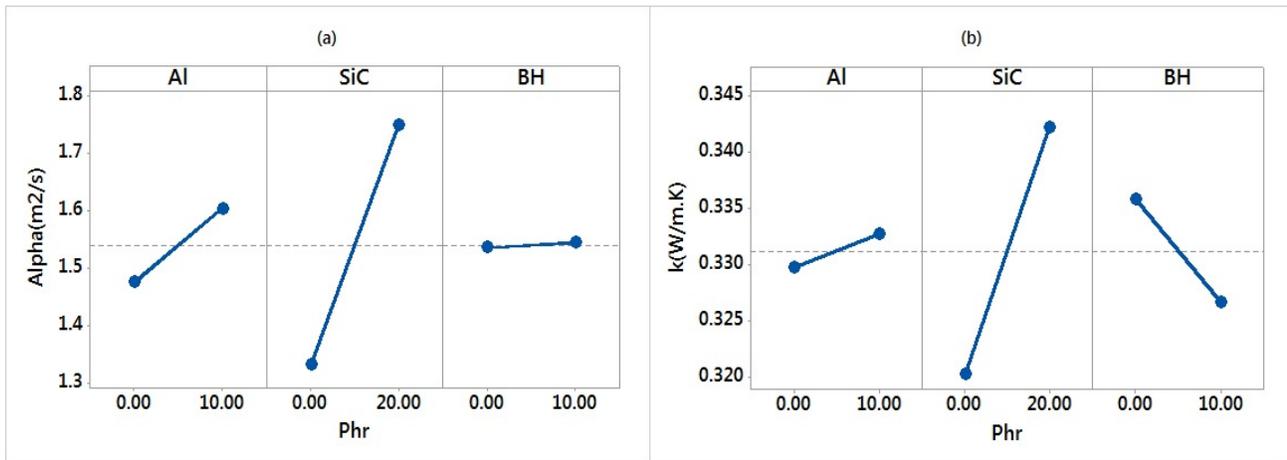


Fig. 5: The main effects plot of ceramic fillers on the properties of thermal diffusivity (Alpha) and heat conductivity (k) of CB-filled butyl rubber

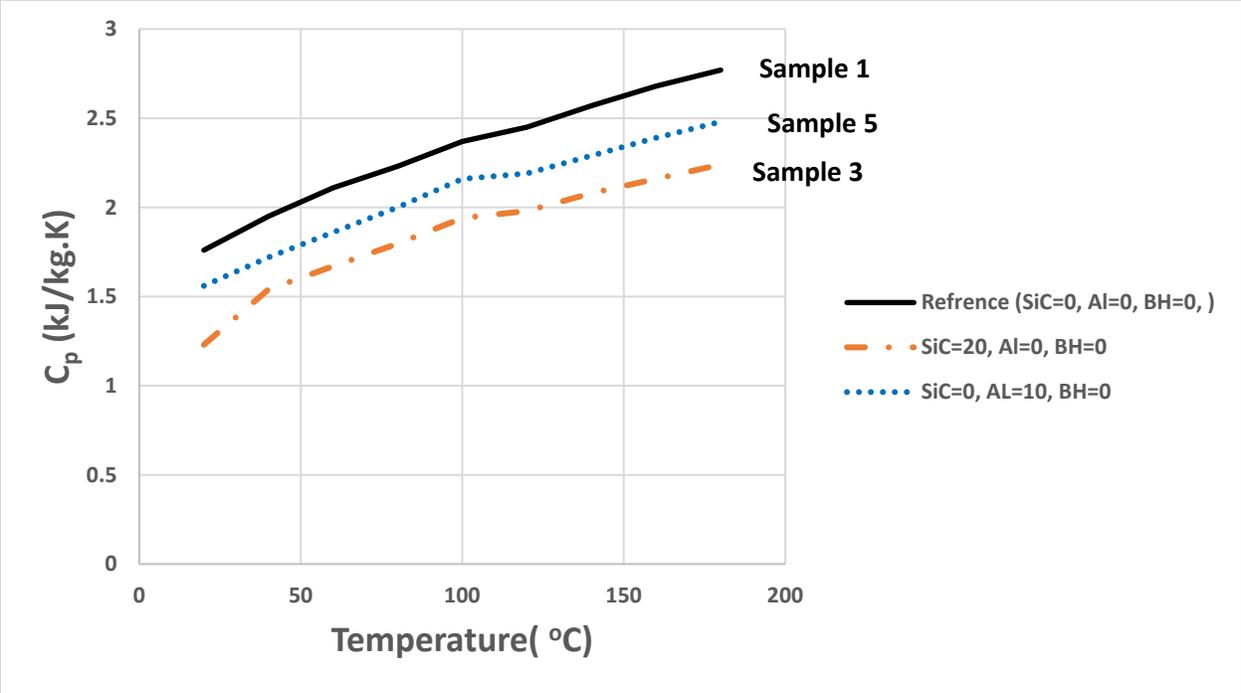


Fig. 6: The specific heat capacity (C_p) of CB, (No. 1), CB/SiC (No. 3) and CB/alumina (No. 5) filled butyl rubber according to the DSC test.

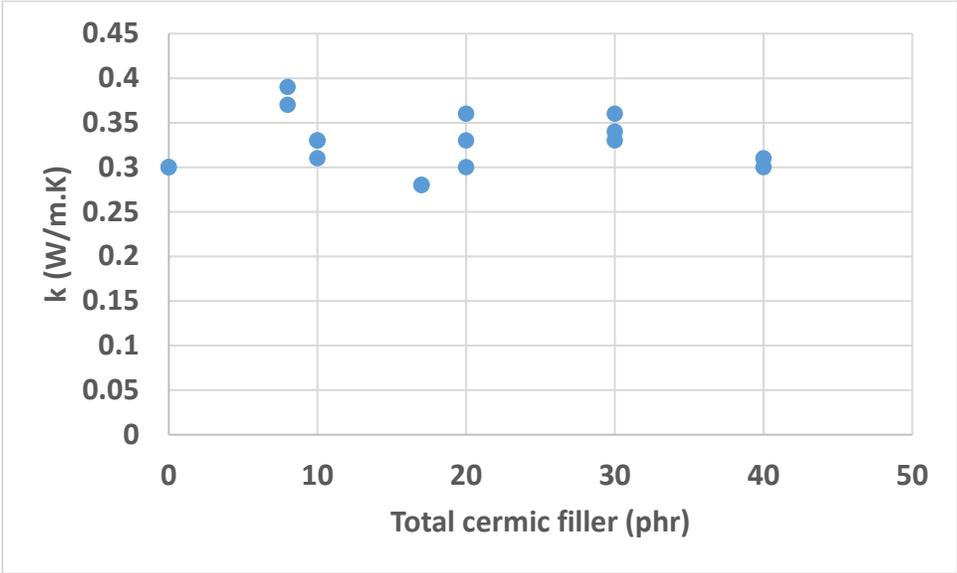


Fig. 7: The effect of total ceramic filler on heat conductivity bladder composite

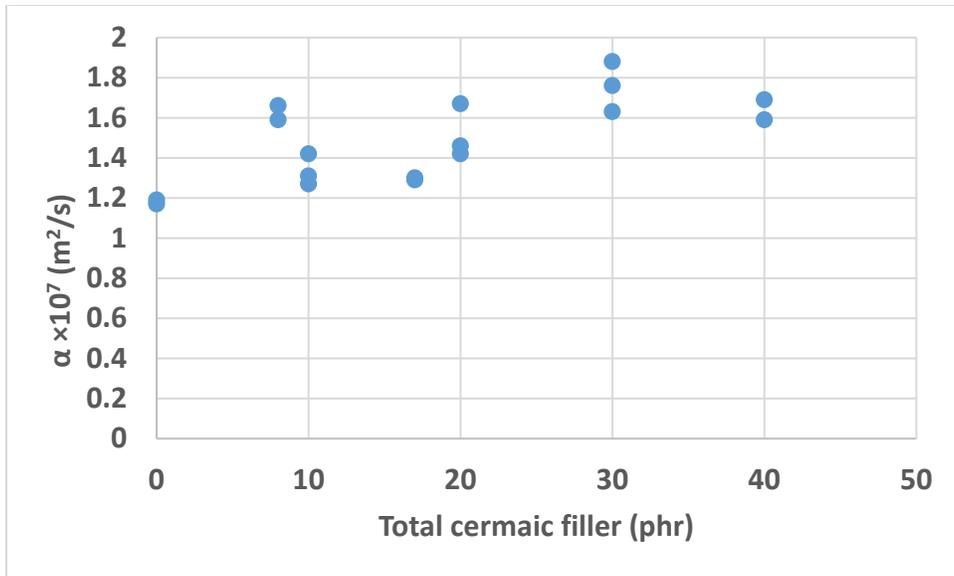


Fig. 8: The effect of total ceramic filler on thermal diffusivity of bladder composite

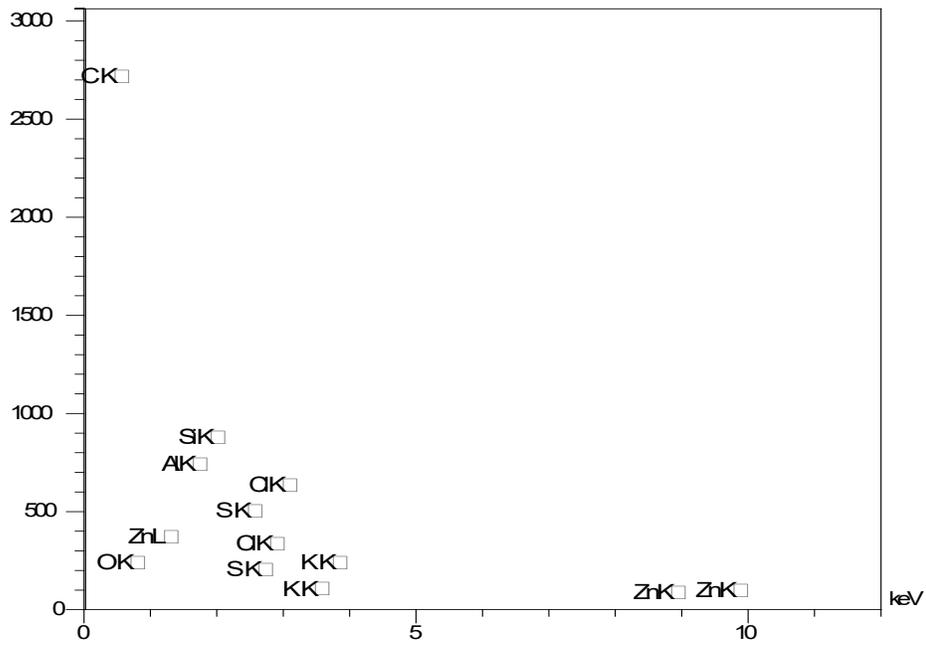
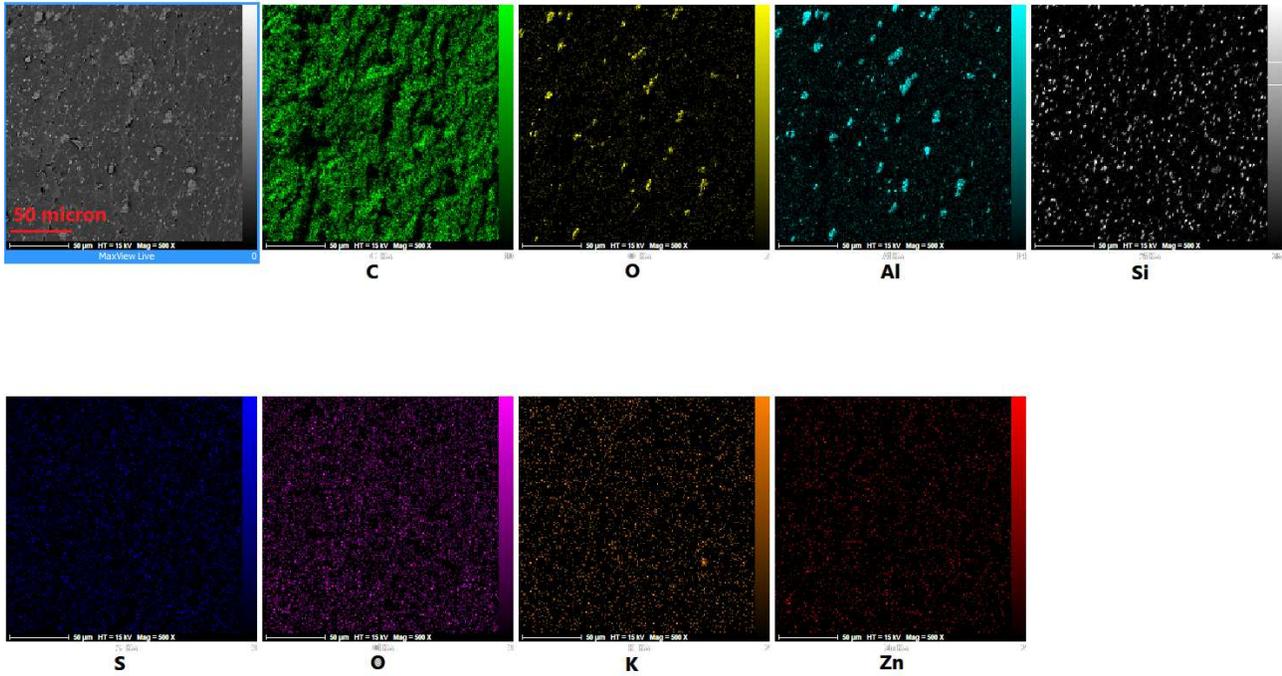


Fig. 9: SEM/MAP and EDS of carbon black filled butyl rubber in the presence of ceramic fillers

References

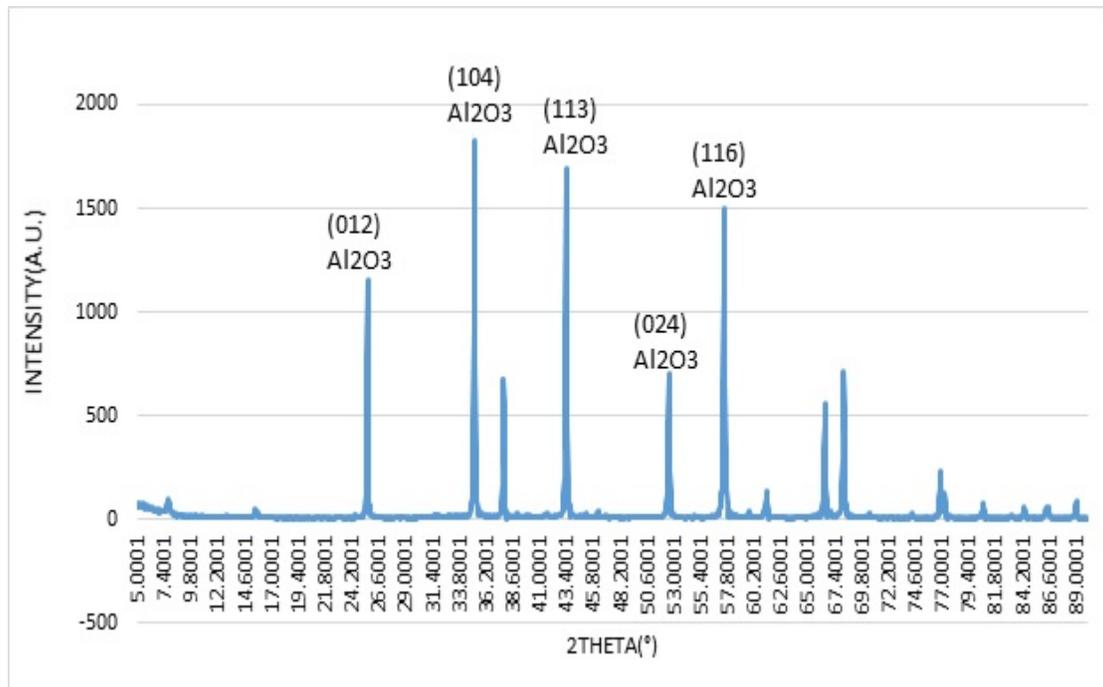
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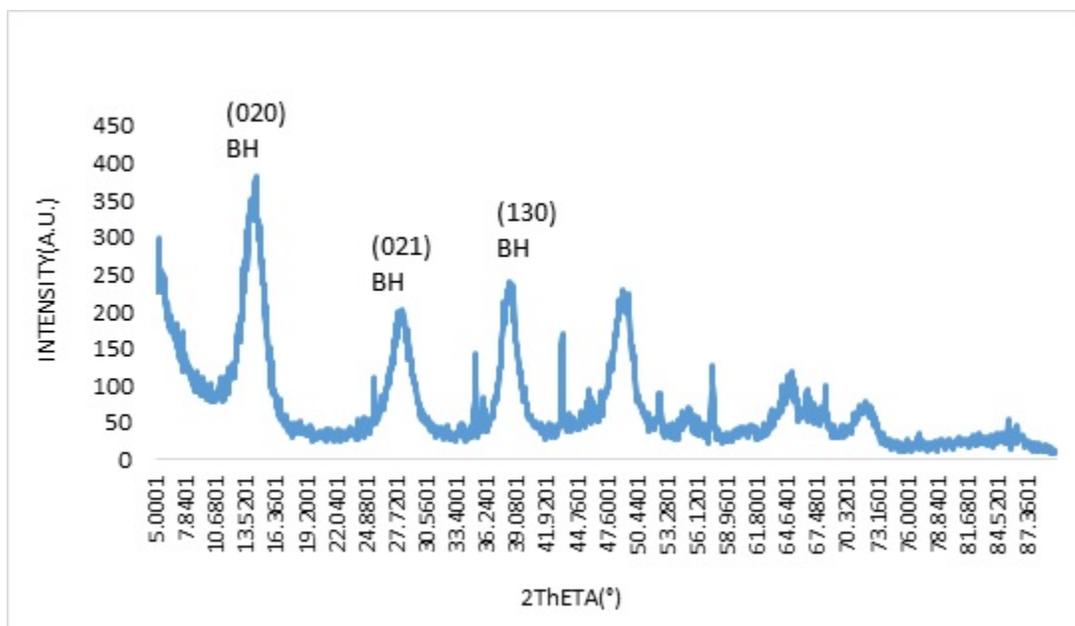
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Appendix: XRD of ceramic fillers

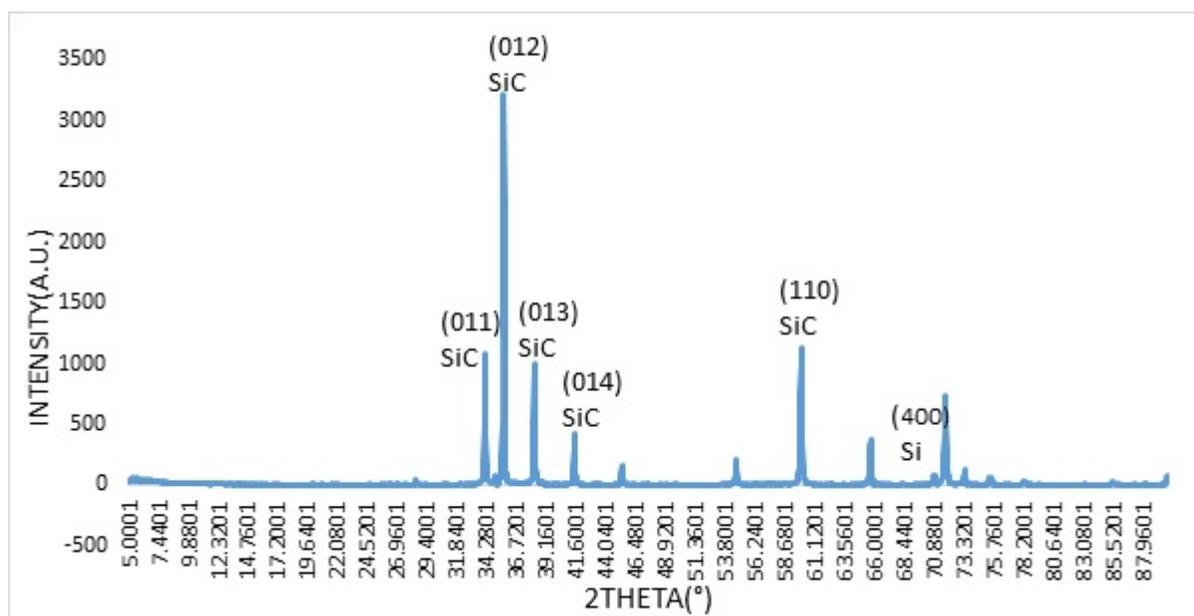
The XRD of alumina, boehmite and silicon carbide are presented here.



(a) XRD of alumina



(b) XRD of boehmite



(c) XRD of SiC

Figures

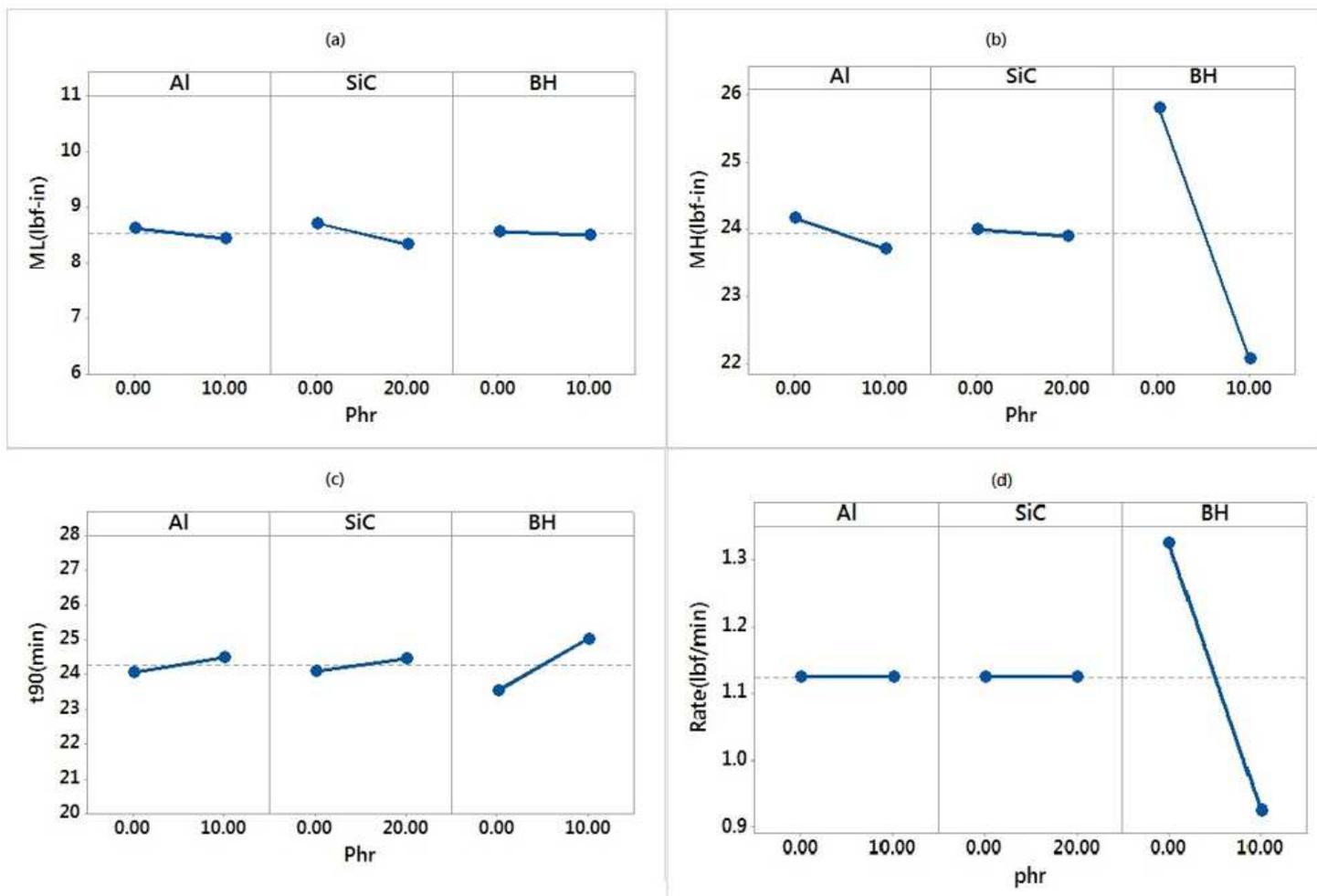


Figure 1

The main effects plot of ceramic fillers on the cure properties of CB-filled butyl rubber

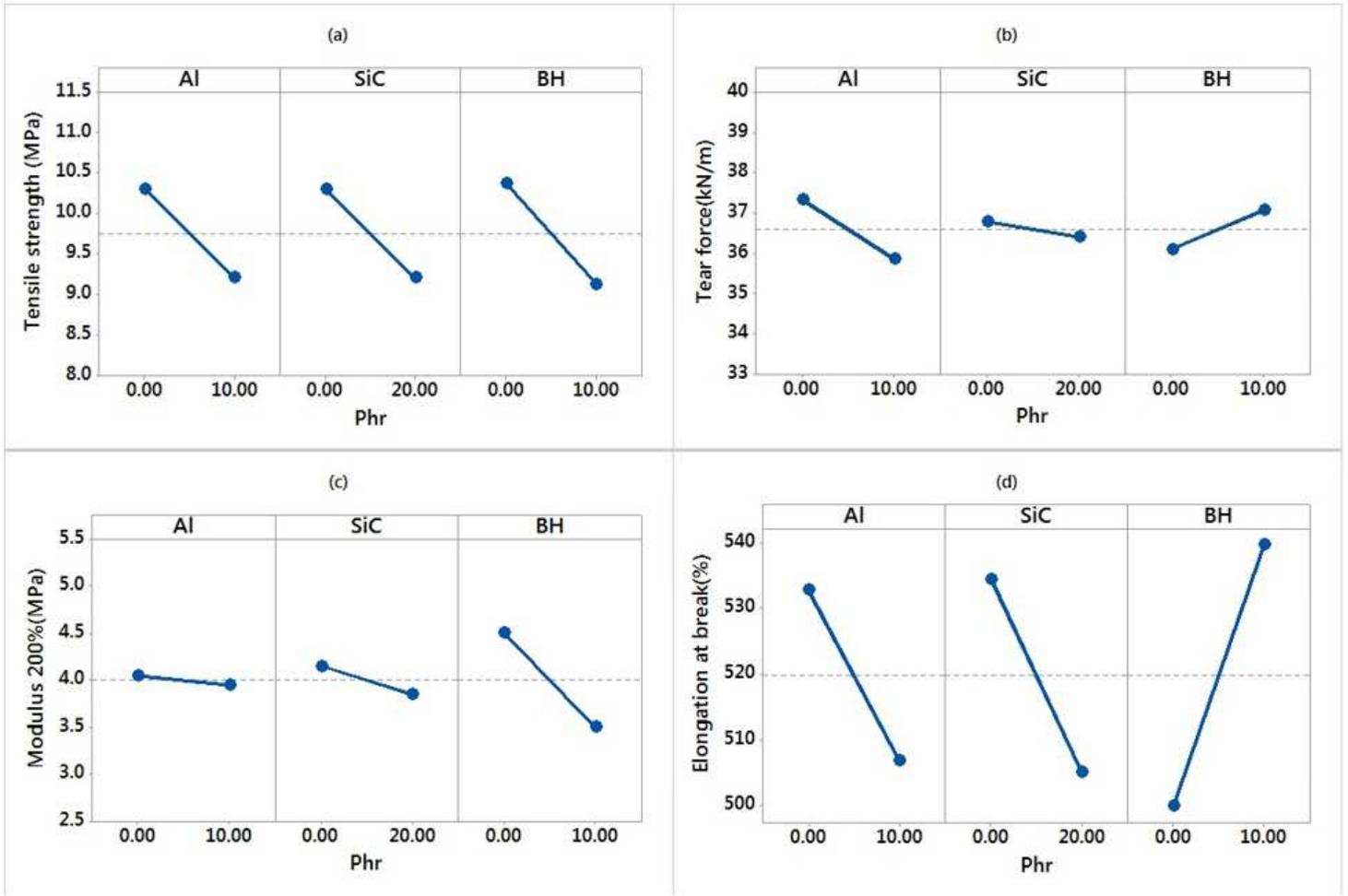


Figure 2

The main effects plot of ceramic fillers on the properties of tensile strength, tear force, modulus 200% and elongation at break of CB-filled butyl rubber

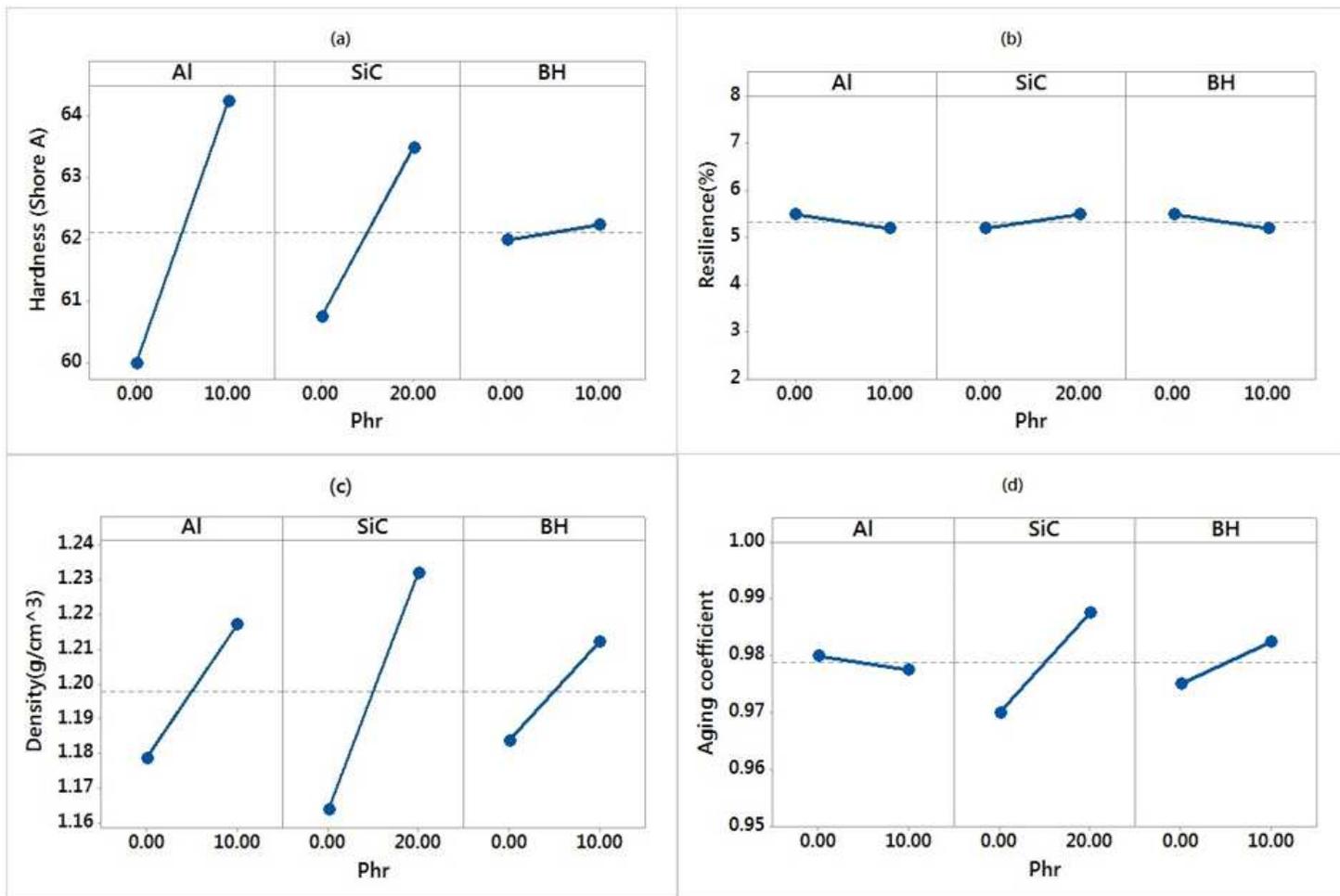


Figure 3

The main effects plot of ceramic fillers on the properties of hardness, resilience, density and aging coefficient of CB-filled butyl rubber

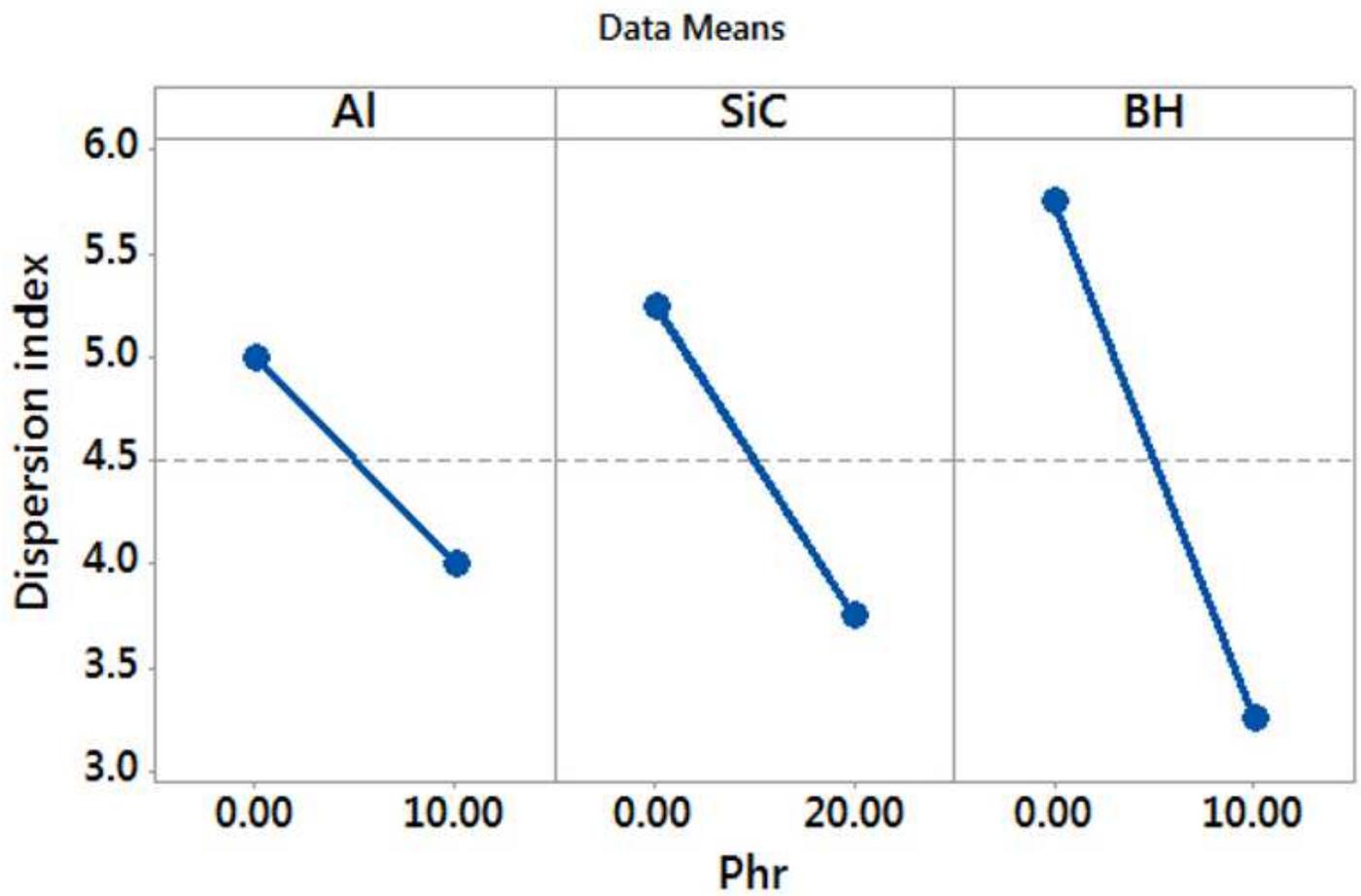


Figure 4

The main effects plot of ceramic fillers on dispersion index of CB-filled butyl rubber

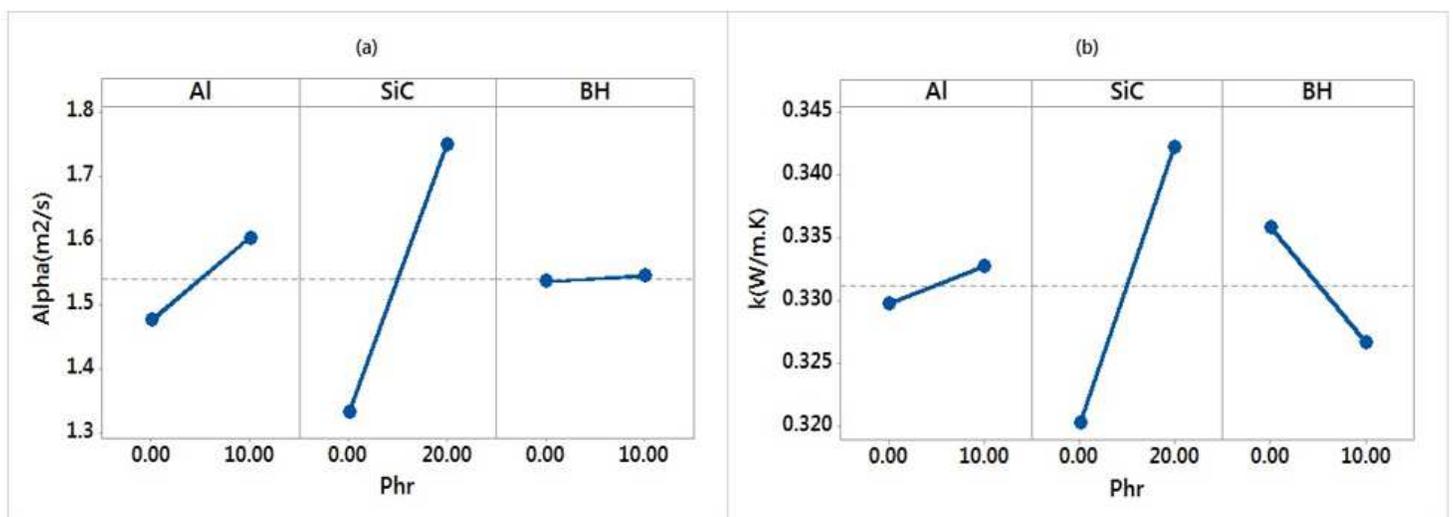


Figure 5

The main effects plot of ceramic fillers on the properties of thermal diffusivity (Alpha) and heat conductivity (k) of CB-filled butyl rubber

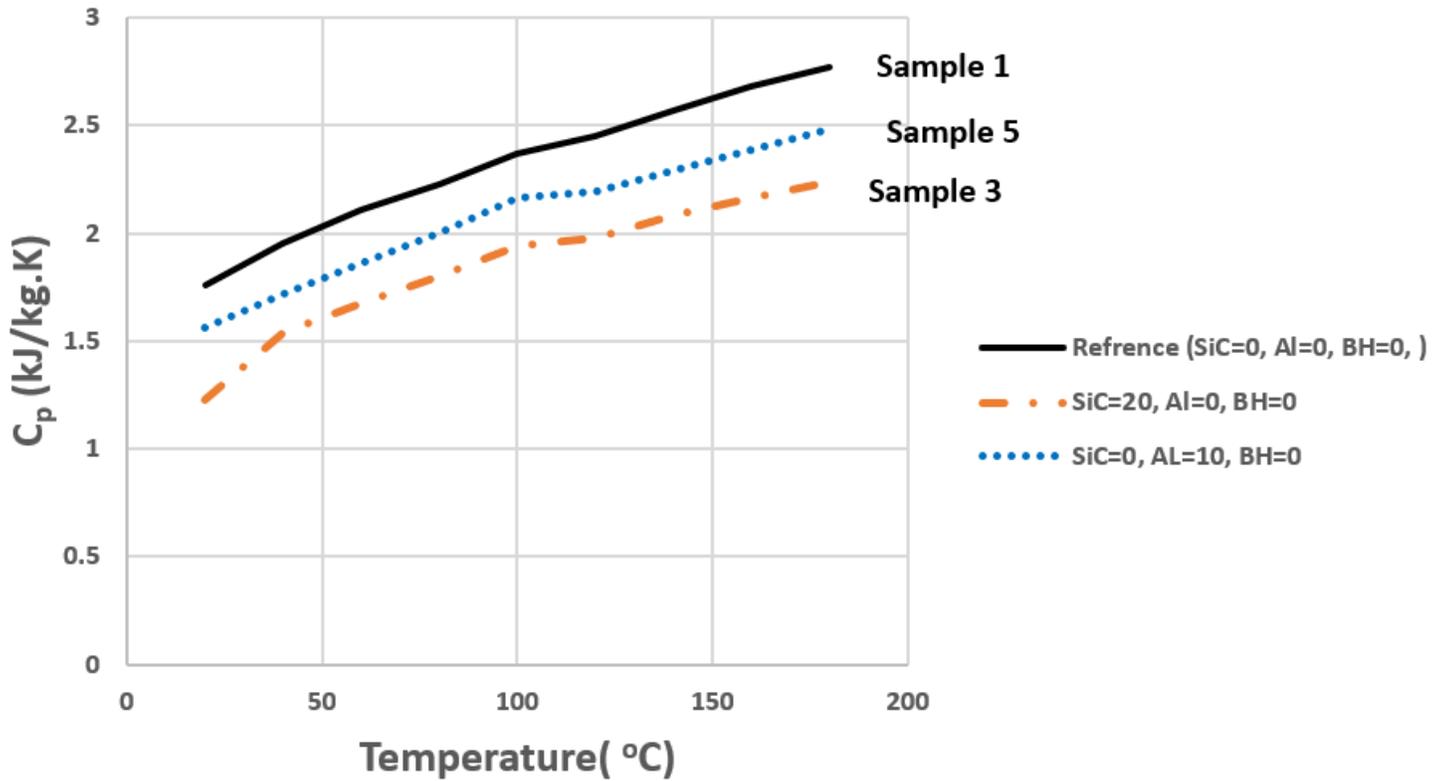


Figure 6

The specific heat capacity (C_p) of CB, (No. 1), CB/SiC (No. 3) and CB/alumina (No. 5) filled butyl rubber according to the DSC test.

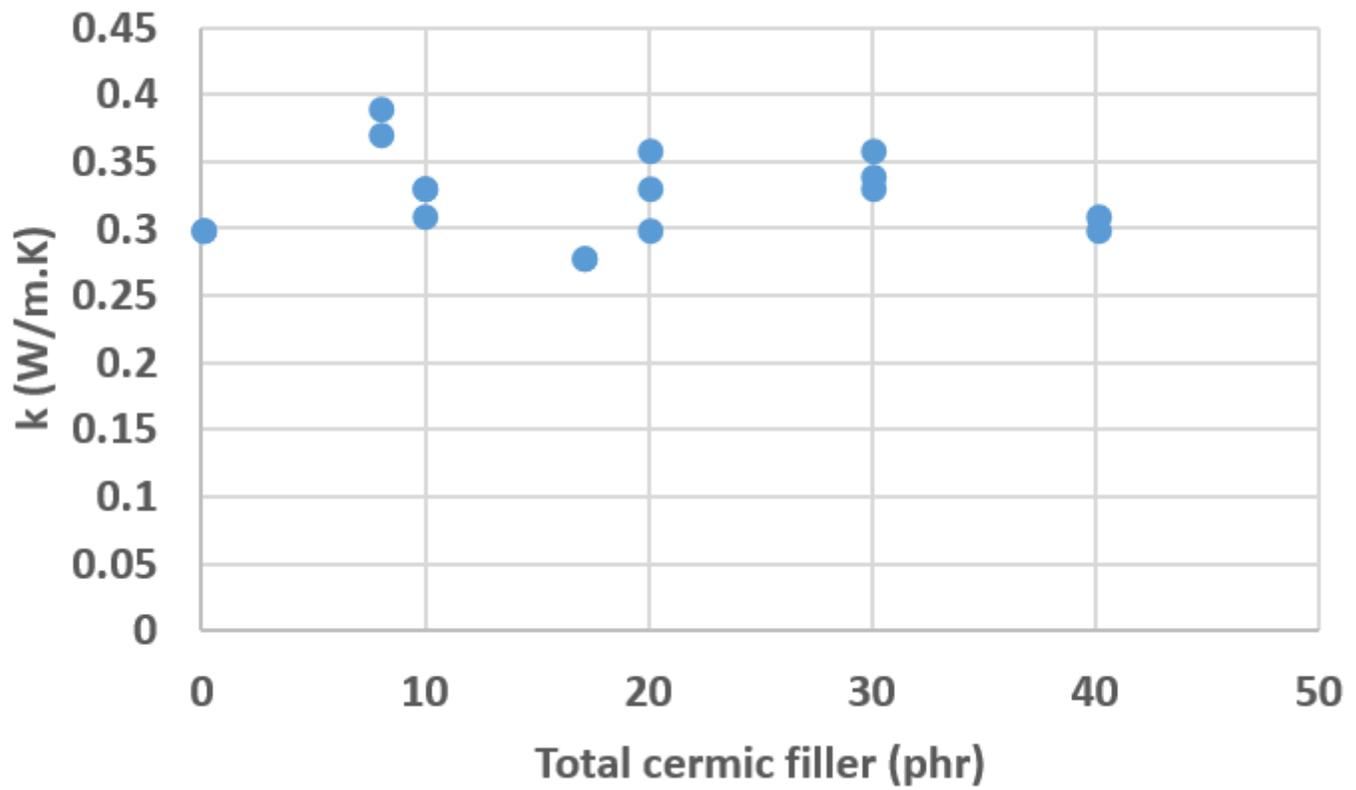


Figure 7

The effect of total ceramic filler on heat conductivity bladder composite

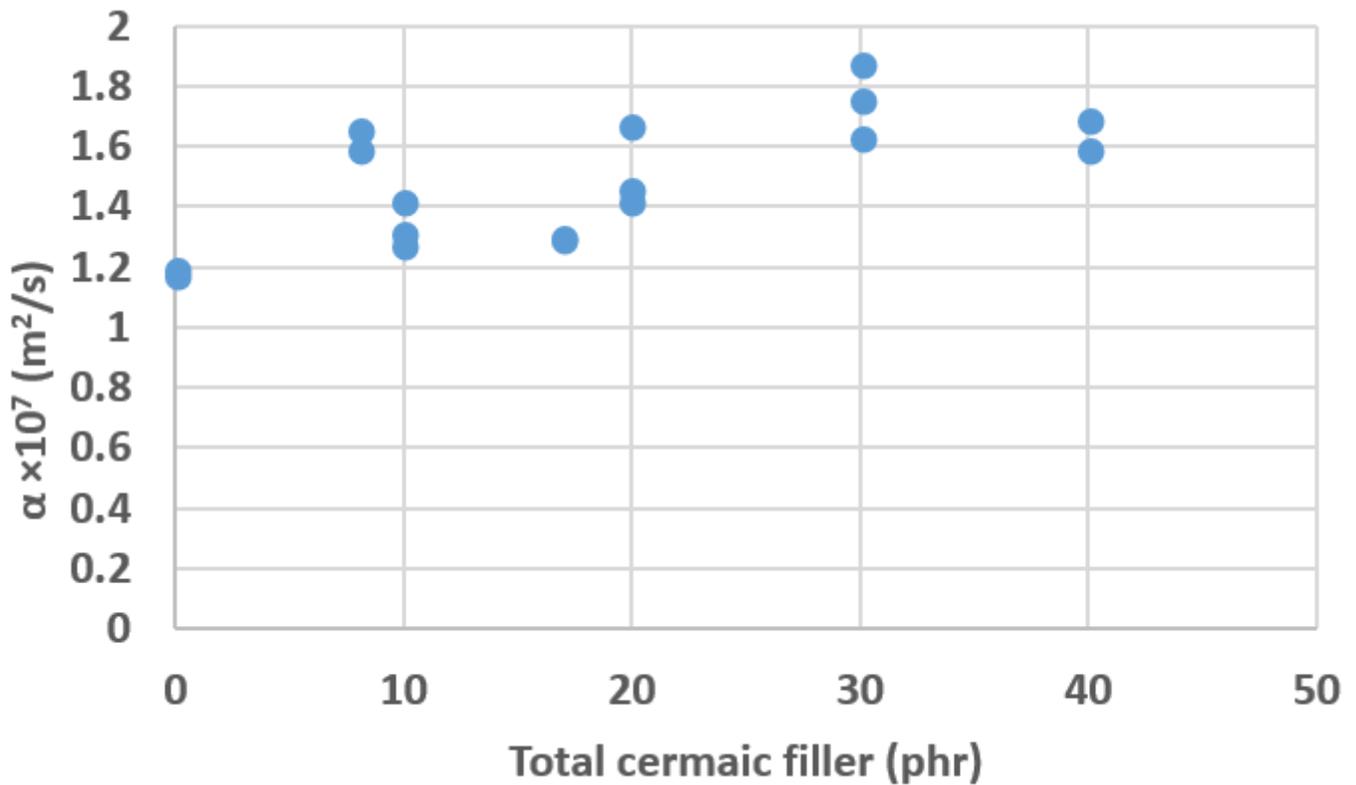


Figure 8

The effect of total ceramic filler on thermal diffusivity of bladder composite

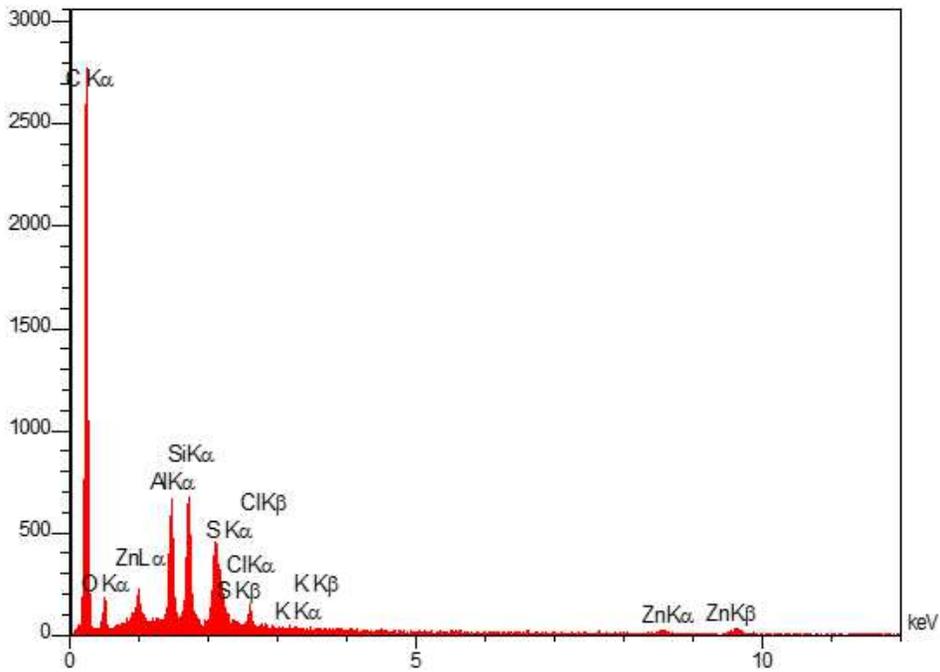
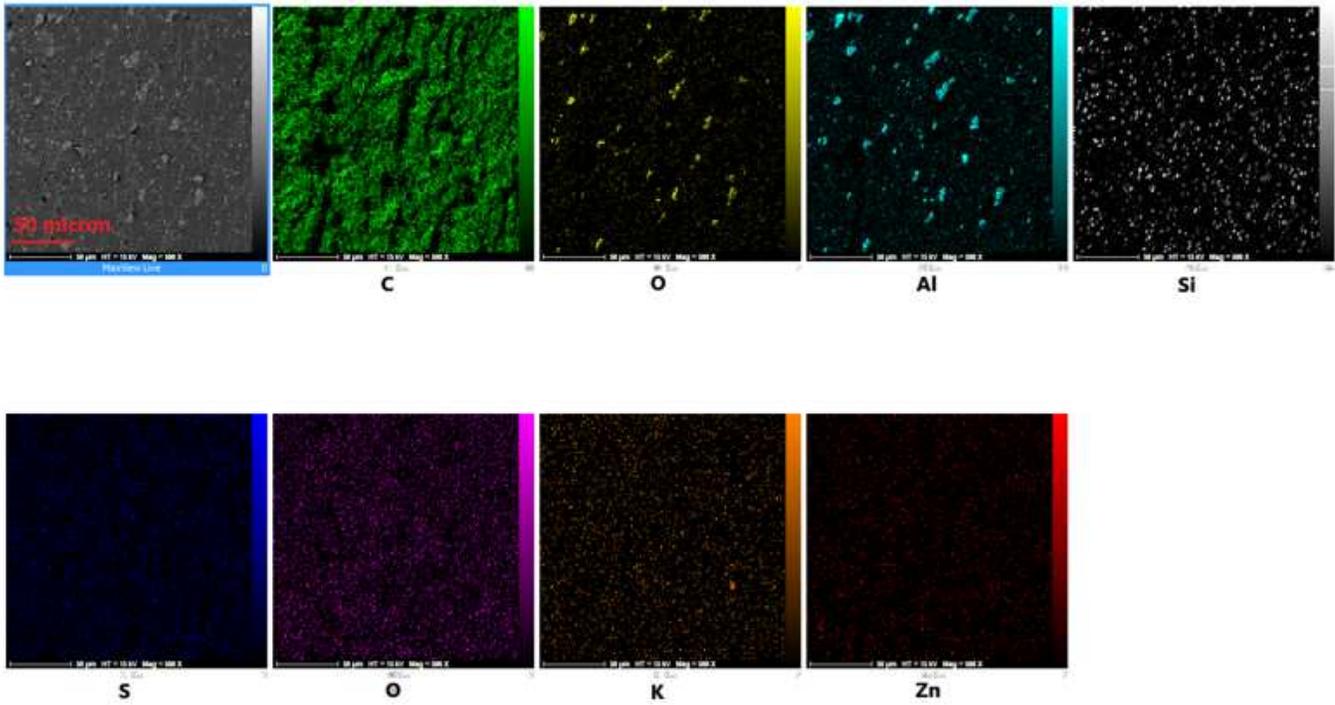


Figure 9

SEM/MAP and EDS of carbon black filled butyl rubber in the presence of ceramic fillers