Tires for Mars Rovers: Reinforcing BR and BR/ Vinyl-Methyl Silicone Rubber Compounds with Carbon Black, Nano-CaCO₃, or Silica for Good Low-Temperature Dynamic-Mechanical Performance

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ABSTRACT: Dynamic increment in Mars exploration missions necessitates the development of new materials that can satisfy the ever more stringent requirements. Currently, most of the materials used for manufacturing Mars rovers and landers are based on various metal alloys that provide high reliability in the Martian environment. However, the future planned missions, including the first human crew landing on Mars, require the development of new rubber materials that could be used for sealing Mars suits, for tires/tracks, and for damping systems for heavy Mars rovers. This research aims to investigate the properties of butadiene rubber (BR) and butadiene/vinyl-methyl silicone rubber blends (BR/VMQ) filled with various reinforcing fillers: carbon blacks (CBs), silicas, and nanometric calcium carbonate (nano-CaCO₃), in order to evaluate their performance from the point of view of Mars' environmental applications. The study revealed that the designed composites exhibit very good lowtemperature elasticity, and the addition of 30 phr of high surface area CB (N220) or silica (Ultrasil 9100) results in good mechanical properties of the compounds. The mechanical properties of the BR/VMQ blends depend on the type of reinforcing filler. The addition of the CBs resulted in better mechanical properties, while the incorporation of silicas worsens the mechanical properties of BR/VMQ blends in comparison to their BR counterparts. The highcis BR grade exhibits a strong tendency to crystallize in the operating temperature range on Mars (crystallization ~ -60 °C, melting ~ -20 °C), and the addition of the fillers nucleates the crystallization, resulting in a higher amount of the crystalline phase. This might be a serious problem for any sealing application of the rubber compounds. For this reason, a noncrystallizable BR grade is recommended for further studies.

KEY WORDS: rubber, Mars, silicone rubber, VMQ, butadiene rubber, BR, carbon black, silica, calcium carbonate

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Introduction

Mars exploration has increased its momentum in recent years significantly. Currently, three rovers and a helicopter are studying the surface of Mars, providing unique research data. Moreover, the future exploration plans are much bolder-from sending a Martian regolith sample back to Earth [1] to the first human landing on Mars [2]. The materials used for Mars missions need to face harsh conditions. First, the travel to Mars, which will take around seven months, takes place in a total vacuum of space and in the presence of solar and galactic radiation at a temperature close to absolute zero (\sim -270 °C). Second, in the mission on Mars' surface, where the temperatures range from -120 °C on a winter night to 30 °C during a summer day, and the UV radiation is much higher than on Earth due to the lack of an ozone layer, the pressure is around 200 times lower than on Earth and frequent dust storms consist of abrasive and sharp regolith particles. In such circumstances, only equipment manufactured from very robust materials can be used for Mars missions. Currently, particular types of metal alloys are used to provide the required performance and reliability. For example, Mars rover wheels are made currently of a thin aluminum sheet that is light in weight and provides reliability. However, since future missions will involve a human crew, other materials have to be developed to resist the Martian environment. This includes new tailor-made polymers, which have not been used on Mars yet. Currently, the Perseverance rover carries a sample box with five polymeric materials, which are under consideration to be used in the new Mars suit development, to investigate their resistance to Martian conditions [3]. However, among these five materials, one particularly important type of polymer is missing-rubber.

Rubber is a unique polymer composite providing high elastic and damping properties simultaneously assuring good mechanical performance. For decades, rubber has been the material of choice to produce tires, seals, hoses, dampers, and many more important engineering elements. In light of the planned crewed mission to Mars, rubber elements are the best materials to provide sealings for Mars suit elements, doors, and airlocks. The shoes need rubber soles to provide comfort of use for astronauts. And finally, Mars rovers capable of crew and cargo transportation have to be equipped with high-performance rubber tires or tracks, and dampers to reduce vibration.

This paper is focused on investigating the effect of the addition of fillers on the properties of butadiene rubber and on silicone/butadiene rubber blends, which contribute to the current RED 4 MARS project [4]. The overall aim of this project is to develop rubber compounds, which can withstand the environmental conditions on Mars. The main critical requirement for rubber materials on Mars will be the ability to provide elastic performance in a broad range of temperatures, much lower than usually present on Earth. Therefore, the rubbers exhibiting the lowest glass transition temperature (T_g) were chosen for the study, namely, butadiene rubber (BR) and vinyl-methyl silicone rubber (VMQ). Silicone rubber provides the lowest T_g of all rubber types, but it lacks good mechanical and wear properties. This can be compensated by the use of BR, which can provide excellent mechanical properties and wear resistance [5].

To achieve the required high performance, rubber compounds need to contain reinforcing fillers. The fillers offering the best properties are currently carbon blacks (CBs) and silicas. They are produced in many types, varying in cluster size and morphology, specific surface area, and surface functionalization [6]. CBs are promising fillers for Mars application because they also improve the radiation [7] and UV resistance [6,8] of rubber compounds, while silica can be chemically extracted from Martian regolith so in the future can be locally produced on Mars, which meets the In Situ Resource Utilization (ISRU) approach [9]. Also, the addition of silica reduces the crack propagation of rubber in rough terrain. In this view, a combination of silica and CB seems to be an optimal two-filler composition. The further questions are-what is the minimum amount of CB assuring a satisfactory UV resistance? And what is the best silica/CB ratio and amount? These questions will be answered in future works. In addition to silica, calcium carbonate also could be synthesized in situ on Mars by using the atmospheric CO_2 and CaO from Mars's regolith. Calcium carbonate might be a promising alternative to CB and silica as a filler for rubber compounds, which is currently intensively studied due to its sustainability, for example, as a reinforcing filler for natural rubber [10]. Like silica, its surface has to be compatibilized for better interaction with rubber to achieve the required performance. One of the compatibilization solutions was recently presented by Moustafa et al., who used a resin enveloping technique [11]. In this study, lipoic acid was used for nano-CaCO₃ compatibilization with rubber, while for silica a state-of-the-art bis(triethoxysilylpropyl)disulfide was used.

To introduce a large amount of reinforcing fillers into rubber, usually processing oils are used. However, the low pressure on Mars would cause the evaporation of such oils (so-called outgassing); therefore, they are not used in the current study. The addition of oils facilitates high filler loading, even up to 80 phr. However, its absence reduces the amount of reinforcing fillers that can be incorporated significantly. In a previous study [12], it was shown that the addition of around 40 phr of CB can be problematic—depending on the CB type. Therefore in the current study, the maximum amount of fillers was limited to 30 phr. The lower amounts (5 phr and 15 phr) of fillers studied in this paper are added to investigate the level needed to reach the percolation threshold and the effect of the presence of the filler on the dynamic-mechanical properties of rubber and its crystallization.

The aim of this study is to improve the mechanical properties of BR and BR/VMQ compounds filled with different amounts and grades of CBs, silicas,

and nano- $CaCO_3$. An emphasis is placed on studying the fillers' influence on the glass transition temperature and on the dynamic and mechanical properties of the compounds. When compounds with sufficient mechanical strength are found, the radiation and UV resistance will be tested in the next step.

Materials and Methods

Materials

A high-cis (>96%) neodymium butadiene rubber (BR)-Buna CB 24 (Arlanxeo, Maastricht, the Netherlands) and a methyl-vinyl silicone rubber (VMQ) containing one vinyl group per 99 methyl groups in the polymer backbone, Polimer MV 1.0 (Silikony Polskie, Nowa Sarzyna, Poland), were used for the preparation of the blends. Carbon black (CB) grades N220, N330, and N550, having specific Brunauer, Emmett and Teller method (BET) surface areas of 114 m²/g, 78 m²/g, and 40 m²/g, respectively, were obtained from MAKROchem (Lublin, Poland). Precipitated silicas Ultrasil 7000 GR and Ultrasil 9100 GR, having specific BET surface areas of 170 m^2/g and 235 m^2/g , respectively, were kindly provided from Evonik Industries (Essen, Germany), while precipitated silica Zeosil 1115 MP, having a specific surface area of 115 m²/g, was kindly provided from Solvay (Brussels, Belgium). Bis(triethoxysilylpropyl)disulfide (TESPD) Si266 was kindly provided from Evonik Industries. Nano-CaCO3 (diameter of 50–100 nm, provided by the producer) was purchased from XFNANO Materials Tech Co., Ltd. (Nanjing, China). The size of the primary particles of the nano-CaCO₃ suggests that its specific surface area is in the range of 30 m²/g, based on a comparison with Semi Reinforcing Furnace CB N770 [13]. Lipoic acid was purchased from Sigma-Aldrich (Schnelldorf, Germany). Zinc oxide, stearic acid, sulfur, N-cyclohexyl-2-benzothiazole sulfenamide (CBS), and N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) were purchased from Caldic B.V. (Rotterdam, the Netherlands).

Preparation of the Samples

The rubber compounds were prepared in a laboratory mixer Plastograph EC (Brabender, Duisburg, Germany), following the procedure presented in Table 1. The compound formulations are presented in Tables 2–7. The amount of TESPD in the silica-filled compounds was adjusted to the weight of the silica without considering its specific surface area to assure similar shear forces during mixing for all the compounds. Liquid TESPD acts as plasticizer on the early stage of mixing, before it reacts chemically with the silica surface, resulting in lowering of the shear forces and thus worsening dispersion of the silica. Also, the amount of lipoic acid was adjusted to the weight fraction of nano-CaCO₃. Lipoic acid melts at 60 °C, which means that it also acts as a plasticizer during mixing. After mixing, the compounds were formed into flat sheets by a two-roll mill, Polymix 80T, Schwabenthan (Berlin, Germany).

Time (min:sec)	Action
Step 1: preheating to 70 °C (2	30 rpm)
0:00	Addition of rubber
1:00	Addition of zinc oxide, stearic acid, and 6PPD
1:30	Addition of the reinforcing filler (CB, silica/silane, or nano-CaCO ₃)
2:00	Increasing the rotor speed to 60 rpm
7:00	Stop mixing (reaching 135–140 °C)
Step 2: preheating to 50 °C (2	30 rpm)
0:00	Addition of the premix from Step 1
0:30	Addition of sulfur, and CBS
1:00	Increasing the rotor speed to 60 rpm
2:00	Stop mixing

TABLE 1 — Mixing procedure of the compounds.

TABLE 2 — Formulation of the BR compounds filled with CBs.

					Samples of	lenotatio	n ^a			
			BR-	BR-		BR-	BR-		BR-	BR-
Component	BR-	BR-	N220-	N220-	BR-	N330-	N330-	BR-	N550-	N550-
(phr)	REF	N220-5	15	30	N330-5	15	30	N550-5	15	30
BR	100	100	100	100	100	100	100	100	100	100
CB N220	_	5	15	30	_	_	_	_	_	_
CB N330	_		_	_	5	15	30	_	_	
CB N550	_		_	_	_	_	_	5	15	30

^aOther ingredients (phr): Activators: zinc oxide, 3; stearic acid, 3. Accelerator: *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS), 1.6. Curative: sulfur, 1.2. Antiozonant: *N*-(1,3-dimethylbutyl)-*N*'-phenyl-*p*-phenylenediamine (6PPD), 2.

				S	amples d	enotatior	n ^a			
			BR-	BR-		BR-	BR-		BR-	BR-
	BR-	BR-	VMQ-	VMQ-	BR-	VMQ-	VMQ-	BR-	VMQ-	VMQ-
Component	VMQ-	VMQ-	N220-	N220-	VMQ-	N330-	N330-	VMQ-	N550-	N550-
(phr)	REF	N220-5	15	30	N330-5	15	30	N550-5	15	30
BR	80	80	80	80	80	80	80	80	80	80
VMQ	20	20	20	20	20	20	20	20	20	20
CB N220	_	5	15	30	_	_	_	_	_	_
CB N330	_	_	_	_	5	15	30	_	_	_
CB N550	—		—	—		—	—	5	15	30

TABLE 3 — Formulation of the BR/VMQ compounds filled with CBs.

^{*a*}Other ingredients (phr): Activators: zinc oxide, 3; stearic acid, 3. Accelerator: *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS), 1.6. Curative: sulfur, 1.2. Antiozonant: *N*-(1,3-dimethylbutyl)-*N*'-phenyl-*p*-phenylenediamine (6PPD), 2.

				Sample	es denota	ution ^a			
		BR-	BR-		BR-	BR-		BR-	BR-
Component	BR-	U9100-	U9100-	BR-	U7000-	U7000-	BR-	Z1115-	Z1115-
(phr)	U9100-5	15	30	U7000-5	15	30	Z1115-5	15	30
BR	100	100	100	100	100	100	100	100	100
Ultrasil 9100 GR	5	15	30	_	_	_	_	_	_
Ultrasil 7000 GR	_	_	_	5	15	30	_	_	_
Zeosil 1115 MP	_	_	_	_	_	_	5	15	30
TESPD	0.5	1.5	3.0	0.5	1.5	3.0	0.5	1.5	3.0

TABLE 4 — Formulation of the BR compounds filled with silica/silane systems.

^aOther ingredients (phr): Activators: zinc oxide, 3; stearic acid, 3. Accelerator: *N*-cyclohexyl-2benzothiazole sulfenamide (CBS), 1.6. Curative: sulfur, 1.2. Antiozonant: *N*-(1,3-dimethylbutyl)-*N*'phenyl-*p*-phenylenediamine (6PPD), 2.

Testing of the Samples

The Payne effect of the unvulcanized compounds was measured by applying strain from 1% to 100% twice. The results from the second sweep were used for the discussion, as the first sweep erases the storage history of the compounds with any potential effect coming from filler flocculation [14]. The testing was done by using MonTech D-RPA 3000 rubber process analyzer, produced by MonTech Werkstoffprüfmaschinen GmbH (Buchen, Germany).

The kinetics of vulcanization of the rubber compounds was measured by the rubber process analyzer RPA elite manufactured by TA Instruments, Waters Corporation (New Castle, Delaware). The tests were done at 160 $^{\circ}$ C with a frequency of 1.67 Hz, and a strain of 9.98% for 30 min.

The rubber compounds were vulcanized in a laboratory hot press (Wickert Maschinenbau GmbH, Landau in der Pfalz, Germany) at 160 °C. This was done

				Sample	es denota	tion ^a			
		BR-	BR-		BR-	BR-		BR-	BR-
	BR-	VMQ-	VMQ-	BR-	VMQ-	VMQ-	BR-	VMQ-	VMQ-
Component	VMQ-	U9100-	U9100-	VMQ-	U7000-	U7000-	VMQ-	Z1115-	Z1115-
(phr)	U9100-5	15	30	U7000-5	15	30	Z1115-5	15	30
BR	80	80	80	80	80	80	80	80	80
VMQ	20	20	20	20	20	20	20	20	20
Ultrasil 9100 GR	5	15	30	_	_	_	_	_	_
Ultrasil 7000 GR	_	_	_	5	15	30	_	_	_
Zeosil 1115 MP	_	_	_	_	_	_	5	15	30
TESPD	0.5	1.5	3.0	0.5	1.5	3.0	0.5	1.5	3.0

TABLE 5 — Formulation of the BR/VMQ compounds filled with silica/silane systems.

^{*a*}Other ingredients (phr): Activators: zinc oxide, 3; stearic acid, 3. Accelerator: *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS), 1.6. Curative: sulfur, 1.2. Antiozonant: *N*-(1,3-dimethylbutyl)-*N*'-phenyl-*p*-phenylenediamine (6PPD), 2.

			Samples de	notation ^a		
				BR-	BR-	BR-
Component	BR-	BR-	BR-	CaCO ₃ -	CaCO ₃ -	CaCO ₃ -
(phr)	CaCO ₃ -5	CaCO ₃ -15	CaCO ₃ -30	$5NoCA^{b}$	15NoCA	30NoCA
BR	100	100	100	100	100	100
Nano-CaCO ₃	5	15	30	5	15	30
Lipoic acid	0.5	1.5	3.0	—	—	—

TABLE 6 — Formulation of the BR compounds filled with nano-CaCO₃.

^aOther ingredients (phr): Activators: zinc oxide, 3; stearic acid, 3. Accelerator: *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS), 1.6. Curative: sulfur, 1.2. Antiozonant: *N*-(1,3-dimethylbutyl)-*N*'-phenyl-*p*-phenylenediamine (6PPD), 2.

^bWithout addition of coupling agent.

according to the results of the kinetics of vulcanization by using the t_{90} parameter, which represents the time to achieve 90% of the torque increase.

The rubber vulcanizates were tested for their mechanical properties using an Instron 5567 tensile tester operating with a crosshead speed of 500 mm/min at room temperature according to ISO 37, Instron Corporation (Norwood, Massachusetts).

Differential scanning calorimetry (DSC) of the vulcanizates was done by DSC 214 Polyma device, Netzsch (Selb, Germany). The scans were carried out in a nitrogen atmosphere with a heating/cooling rate of 20 °C/min, ranging from -140 °C to 20 °C.

Dynamic mechanical analysis (DMA) of the vulcanizates was performed by means of Gabo Eplexor 2500 DMA operating in a tensile mode from -140°C to 20 °C with a heating rate of 3 °C/min, according to ISO 6721-11.

Results and Discussion

The low temperatures on Mars necessitate the application of low glass transition temperature (T_g) rubbers that can assure the flexibility of the functional rubber elements, like tires, hoses, or seals. To achieve this, only two rubber types currently available on the market are suitable: (1) butadiene rubber

		Samples denotation ^a	
Component (phr)	BR-VMQ-CaCO ₃ -5	BR-VMQ- CaCO ₃ -15	BR-VMQ-CaCO3-30
BR	80	80	80
VMQ	20	20	20
Nano-CaCO ₃	5	15	30
Lipoic acid	0.5	1.5	3.0

TABLE 7 — Formulation of the BR/VMQ compounds filled with nano-CaCO₃.

^aOther ingredients (phr): Activators: zinc oxide, 3; stearic acid, 3. Accelerator: *N*-cyclohexyl-2benzothiazole sulfenamide (CBS), 1.6. Curative: sulfur, 1.2. Antiozonant: *N*-(1,3-dimethylbutyl)-*N*'phenyl-*p*-phenylenediamine (6PPD), 2.

(BR), which exhibits the lowest T_{g} of all organic rubbers, and has good mechanical properties and wear resistance, while its UV resistance is rather poor; (2) silicone rubber (VMQ), which is characterized by the lowest T_{g} of all rubber types, has a good UV resistance, but shows inferior mechanical and wear performance compared with organic rubbers like BR. To combine the advantages of both rubber types and reduce their drawbacks, blends of BR/ VMQ are introduced, in which BR is the continuous phase and VMQ is the dispersed phase. Due to relatively low intermolecular interactions, rubbers are rarely used without reinforcing fillers. In this work, the BR compounds and BR/ VMQ blends are filled with various grades of state-of-the-art reinforcing fillers-silica and carbon black, and an experimental nanometric grade of calcium carbonate, which has the potential to be in situ produced on the Mars surface. The effect of the filler types and amounts on the rubber blends processing, microstructure, and dynamic and mechanical properties was investigated. Because BR exhibits better mechanical properties than VMQ, the BR compounds without the addition of VMQ are used as internal references showing the full mechanical and dynamic potential of butadiene rubber, in comparison to which the VMQ/BR blends were tested.

Payne Effect

The Payne effect measurements give information about the filler-filler and filler-rubber interactions in filled rubber compounds [15]. The decrease of storage modulus in the function of strain ($\Delta G'$) is often associated with fillerfiller interactions, while the value of the storage modulus at the maximum strain indicates filler-rubber interactions. However, the Payne effect-related decrease of G' with increasing strain needs to be separated from the strain-induced softening of pure rubber, which is not related to the filler-filler and filler-rubber interactions but results from disentanglements of rubber molecules and configurational changes of the rubber-molecular network caused by the increasing strain, which cannot be reformed immediately [16]. Different rubber grades exhibit different linearity regions, within which the Payne effect can be measured. Therefore, the unfilled compounds (BR-REF and RB-VMQ-REF) were measured first to investigate the rubber linearity region (Figure 1), which is noticeable up to 20% of strain for both compounds. Based on these results, the Payne effect was calculated as the G' difference between 1% and 20% of strain. Subsequently, to discuss filler–rubber interactions the G' value at 20% of elongation is used.

The Payne effect results for the unvulcanized compounds are presented in Tables 8–13 along with their kinetics of vulcanization and mechanical properties of the vulcanizates. The $\Delta G'$ value increases with an increase in the filler loading, which is a well-known phenomenon and stems from increasing interactions between the filler clusters. The Payne effect is observed even for the compounds containing relatively low amounts of the fillers, 5 phr,



FIG. 1 — Changes to storage modulus in the function of strain for the reference samples.

and 15 phr, which are barely sufficient to form a strong filler network. This can be explained by the contribution of adsorption/desorption of rubber macromolecules on/from the filler surface. This is known as Dannenberg's molecular slippage model and is a vital part of the Payne effect [17]. Nevertheless, when the filler content reaches 30 phr, the $\Delta G'$ value increases significantly due to a sufficient filler structure formation, resulting from passing the percolation threshold. This is especially visible for the N220 carbon black and Ultrasil9100 silica, which have the highest specific surface area and exhibit the strongest reinforcing potential from all the tested fillers. As an example, the G' changes with an increasing strain of BR compounds filled with N220 are shown in Figure 2.

Interestingly, a higher Payne effect is noticed for the BR/VMQ blends in comparison to BR compounds containing the same type and amount of filler. This suggests that the fillers are preferably located in one rubber phase, which causes a decrease in the mean distance between filler clusters, resulting in increased filler-filler interactions. Also, the filler network breaks down much faster in BR/VMQ blends than in BR. In contrast to the expectations mentioned above, the Payne effect values for the BR/VMQ blends are higher in comparison to their BR counterparts for all the filler types and amounts, suggesting that the BR/VMQ blends can reach better mechanical properties than just BR-based compounds. This might be an effect of the preferential location of the filler in one polymer phase that results in less homogeneous filler distribution in the bulk of the blend leading to higher susceptibility of the network to a strain-induced breakdown. Alternatively, this also might be caused by the accumulation of filler particles in the BR/VMQ interphase. Such an effect is known for incompatible polymer blends [18]. However, these are just hypotheses, and further studies must be done to investigate this phenomenon in

					Samples c	lenotation				
	BR-	BR-	BR-	BR-	BR-	BR-	BR-	BR-	BR-	BR-
Property	REF	N220-5	N220-15	N220-30	N330-5	N330-15	N330-30	N550-5	N550-15	N550-30
Kinetics of vulcani	zation									
S'_{\min} (dNm)	1.1	1.2	1.5	2.2	1.1	1.4	2.0	1.2	1.5	2.0
$S'_{\rm max}$ (dNm)	12.5	14.0	16.0	20.8	13.5	16.6	19.7	13.6	17.4	21.3
t_{02} (min)	5.0	4.0	3.5	3.1	3.7	3.0	2.5	4.3	3.3	2.8
t_{90} (min)	19.1	11.2	10.5	9.7	10.9	8.4	8.4	13.3	8.8	8.1
Payne effect										
$\Delta G'$ (kPa)	0.0	6.7	13.1	52.6	5.3	10.4	35.0	5.8	11.6	27.0
G' @ 20% (kPa)	125.4	136.9	169.3	223.9	128.5	158.0	216.5	136.5	163.7	215.8
Mechanical propert	ies									
Ts (MPa)	1.3 ± 0.1	1.9 ± 0.1	3.7 ± 0.6	8.9 ± 1.7	2.2 ± 0.1	3.2 ± 0.3	7.0 ± 0.3	2.2 ± 0.2	3.7 ± 0.2	6.3 ± 0.9
Eb~(%)	120 ± 12	203 ± 11	278 ± 27	345 ± 40	257 ± 10	230 ± 19	282 ± 13	202 ± 20	235 ± 10	246 ± 27

TABLE 8 — Kinetics of vulcanization, Payne effect, and mechanical properties of BR compounds filled with CBs.

	ABLE 9 — 1	VINEUCS OF VUICE	anizanon, Fay	ne ejjeci, ana	теспатсан р	nopernes of B	клищи сотр	ounas Julea w	UIN CBS.	
					Samples d	lenotation				
	BR-VMQ-	BR-VMQ-	BR-VMQ-	BR-VMQ-	BR-VMQ-	BR-VMQ-	BR-VMQ-	BR-VMQ-	BR-VMQ-	BR-VMQ-
Property	REF	N220-5	N220-15	N220-30	N330-5	N330-15	N330-30	N550-5	N550-15	N550-30
Kinetics of vulcani	zation									
S'_{\min} (dNm)	0.6	0.7	1.1	1.9	0.7	1.0	1.6	0.7	1.0	1.7
$S'_{\rm max}$ (dNm)	9.2	9.9	12.9	17.1	10.1	12.6	16.4	10.8	13.2	17.6
t_{02} (min)	3.9	2.2	2.1	1.8	2.0	1.4	1.0	2.6	1.9	1.6
t_{90} (min)	9.7	8.1	6.2	6.5	5.9	4.4	4.2	7.1	5.6	5.7
Payne effect										
$\Delta G'$ (kPa)	0.0	4.0	22.5	119.5	1.4	17.5	71.4	1.3	11.9	48.5
G' @ 20% (kPa)	81.3	93.8	123.2	178.4	88.7	117.7	163.5	94.2	121.6	176.0
Mechanical proper	ties									
Ts (MPa)	1.5 ± 0.2	$1.5\pm <\!0.1$	3.9 ± 0.2	9.2 ± 0.1	1.5 ± 0.1	3.0 ± 0.1	7.1 ± 0.7	1.7 ± 0.1	3.3 ± 0.3	6.9 ± 0.5
Eb (%)	245 ± 37	183 ± 6	286 ± 8	341 ± 2	181 ± 22	231 ± 5	309 ± 20	185 ± 20	235 ± 34	272 ± 17

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Froperty U9100-5 U9100-15 U9100-50 L1115-5 Kinetics of vulcanization $3'_{min}$ (dNm) 1.3 1.9 3.0 1.3 1.1 2.5 1.1 $5'_{max}$ (dNm) 1.3 1.9 3.0 1.3 1.7 2.5 1.1 $5'_{max}$ (dNm) 13.5 17.5 18.3 13.4 16.0 20.8 12.9 $5'_{max}$ (dNm) 5.3 4.9 2.3 5.1 5.1 4.2 4.8 f_{02} (min) 5.1 2.0.3 20.7 22.3 20.3 Payne effect 7.9 18.0 5.3.7 9.2 15.1.6 18.9 24.1 $\Delta G'$ (kPa) 7.9 18.0 53.7 9.2 12.9 39.3 4.1 $\Delta G'$ (kPa) 7.9 18.0 53.7 9.2 12.9 39.3 4.1 $\Delta G'$ (kPa) 155.8 204.8 268.3 151.6 188.9 242.0 142.6 Mechanical properties 2.3 \pm 0.3 </th <th>ſ</th> <th>BR-</th> <th>BR-</th> <th>BR-</th> <th>BR-</th> <th>BR-</th> <th>BR-</th> <th>BR-</th> <th>BR-</th> <th>BR-</th>	ſ	BR-	BR-	BR-	BR-	BR-	BR-	BR-	BR-	BR-
Kinetics of vulcanization S'_{\min} (dNm)1.31.93.01.31.72.51.1 S'_{\min} (dNm)13.517.518.313.416.020.812.9 S'_{\max} (dNm)5.34.92.35.15.14.24.8 T_{02} (min)5.34.92.35.15.14.24.8 T_{02} (min)20.120.523.520.320.722.320.3Payne effect7.918.053.79.212.939.34.1 $\Delta G'$ (kPa)7.918.053.79.212.939.34.1 $\Delta G'$ (kPa)155.8204.8268.3151.6188.9242.0142.6Mechanical properties2.3 \pm 0.33.1 \pm 0.49.8 \pm 0.52.0 \pm 0.13.5 \pm 0.48.7 \pm 1.02.2 \pm 0.3Ts (MPa)2.61 \pm 45293 \pm 38564 \pm 13193 \pm 16286 \pm 24431 \pm 46244 \pm 31	Property	U9100-5	U9100-15	U9100-30	U7000-5	U7000-15	U7000-30	Z1115-5	Z1115-15	Z1115-30
	Cinetics of vulcanization	on								
	S'_{\min} (dNm)	1.3	1.9	3.0	1.3	1.7	2.5	1.1	1.4	2.0
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$S'_{\rm max}$ (dNm)	13.5	17.5	18.3	13.4	16.0	20.8	12.9	15.8	20.4
t_{90} (min) 20.1 20.5 23.5 20.3 20.7 22.3 20.3 Payne effect 7.9 18.0 53.7 9.2 12.9 39.3 4.1 $\Delta G'$ (kPa) 7.9 18.0 53.7 9.2 12.9 39.3 4.1 $\Delta G'$ (kPa) 155.8 204.8 268.3 151.6 188.9 242.0 142.6 Mechanical properties 3.1 ± 0.4 9.8 ± 0.5 2.0 ± 0.1 3.5 ± 0.4 8.7 ± 1.0 2.2 ± 0.3 Ts (MPa) 2.61 \pm 45 293 ± 38 564 \pm 13 193 \pm 16 286 ± 24 431 \pm 46 244 \pm 31	t_{02} (min)	5.3	4.9	2.3	5.1	5.1	4.2	4.8	5.5	5.6
Payne effectPayne effect $\Delta G'$ (kPa)7.918.053.79.212.939.34.1 $\Delta G'$ (kPa)155.8204.8268.3151.6188.9242.0142.6 G' (@20% (kPa)155.8204.8268.3151.6188.9242.0142.6Mechanical properties T_S (MPa) 2.3 ± 0.3 3.1 ± 0.4 9.8 ± 0.5 2.0 ± 0.1 3.5 ± 0.4 8.7 ± 1.0 2.2 ± 0.3 T_S (MPa) 261 ± 45 293 ± 38 564 ± 13 193 ± 16 286 ± 24 431 ± 46 244 ± 31	t_{90} (min)	20.1	20.5	23.5	20.3	20.7	22.3	20.3	19.9	20.5
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	ayne effect									
$G'(@20\%$ (kPa) 155.8 204.8 268.3 151.6 188.9 242.0 142.6 Mechanical properties T_S (MPa) 2.3 ± 0.3 3.1 ± 0.4 9.8 ± 0.5 2.0 ± 0.1 3.5 ± 0.4 8.7 ± 1.0 2.2 ± 0.3 Eb (\%) 261 ± 45 293 ± 38 564 ± 13 193 ± 16 286 ± 24 431 ± 46 244 ± 31	$\Delta G'$ (kPa)	7.9	18.0	53.7	9.2	12.9	39.3	4.1	9.6	28.9
Mechanical properties Ts (MPa) 2.3 ± 0.3 3.1 ± 0.4 9.8 ± 0.5 2.0 ± 0.1 3.5 ± 0.4 8.7 ± 1.0 2.2 ± 0.3 Eb (\%) 261 ± 45 293 ± 38 564 ± 13 193 ± 16 286 ± 24 431 ± 46 244 ± 31	G' @ 20% (kPa)	155.8	204.8	268.3	151.6	188.9	242.0	142.6	168.7	213.5
Ts (MPa) 2.3 ± 0.3 3.1 ± 0.4 9.8 ± 0.5 2.0 ± 0.1 3.5 ± 0.4 8.7 ± 1.0 2.2 ± 0.3 Eb (%) 261 ± 45 293 ± 38 564 ± 13 193 ± 16 286 ± 24 431 ± 46 244 ± 31	Aechanical properties									
Eb (%) 261 ± 45 293 ± 38 564 ± 13 193 ± 16 286 ± 24 431 ± 46 244 ± 31	Ts (MPa)	2.3 ± 0.3	3.1 ± 0.4	9.8 ± 0.5	2.0 ± 0.1	3.5 ± 0.4	8.7 ± 1.0	2.2 ± 0.3	2.7 ± 0.6	8.4 ± 0.4
	Eb (%)	261 ± 45	293 ± 38	564 ± 13	193 ± 16	286 ± 24	431 ± 46	244 ± 31	238 ± 54	369 ± 17

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				Se	mples denotation				
Property	BR-VMQ- U9100-5	BR-VMQ- U9100-15	BR-VMQ- U9100-30	BR-VMQ- U7000-5	BR-VMQ- U7000-15	BR-VMQ- U7000-30	BR-VMQ- Z1115-5	BR-VMQ- Z1115-15	BR-VMQ- Z1115-30
Kinetics of vulcaniz	ation								
S'_{\min} (dNm)	0.9	1.7	3.7	0.9	1.6	2.9	0.9	1.3	2.1
$S'_{\rm max}$ (dNm)	11.5	16.1	20.7	11.3	15.9	22.0	10.7	15.1	21.0
t_{02} (min)	4.5	4.9	3.7	4.9	5.2	4.4	4.9	4.7	4.0
t_{90} (min)	11.1	12.4	15.4	12.6	12.4	12.7	12.5	11.3	10.7
Payne effect									
$\Delta G'$ (kPa)	6.8	27.5	128.8	4.2	24.4	84.7	7.5	14.8	50.9
G' @ 20% (kPa)	111.9	178.7	278.6	107.7	161.4	242.9	103.2	137.8	185.5
Mechanical properti	es								
Ts (MPa)	$1.3\pm <\!0.1$	2.4 ± 0.1	7.7 ± 1.1	1.2 ± 0.1	$2.2\pm <\!\!0.1$	5.3 ± 0.3	1.5 ± 0.1	2.6 ± 0.3	5.7 ± 1.1
Eb (%)	164 ± 7	256 ± 12	493 ± 46	116 ± 27	201 ± 10	300 ± 17	173 ± 26	220 ± 27	272 ± 46

TABLE 11 — Kinetics of vulcanization, Payne effect, and mechanical properties of BRVMQ compounds filled with silical systems.

		Samples denotation					
				BR-	BR-	BR-	
	BR-	BR-	BR-	CaCO ₃ -	CaCO ₃ -	CaCO ₃ -	
Property	CaCO ₃ -5	CaCO ₃ -15	CaCO ₃ -30	5NoCA	15NoCA	30NoCA	
Kinetics of vulcaniz	zation						
S'_{\min} (dNm)	1.1	1.1	1.2	1.0	1.1	1.2	
$S'_{\rm max}$ (dNm)	13.3	13.8	14.4	12.8	13.7	15.0	
<i>t</i> ₀₂ (min)	4.4	4.6	4.2	4.3	3.5	3.6	
<i>t</i> ₉₀ (min)	15.0	16.5	14.0	10.7	9.6	9.5	
Payne effect							
$\Delta G'$ (kPa)	10.4	7.7	17.1	5.1	7.4	16.6	
G'@20% (kPa)	120.3	128.0	136.4	115.4	123.5	132.7	
Mechanical propert	ies						
Ts (MPa)	1.5 ± 0.1	$1.5 \pm < 0.1$	2.2 ± 0.1	1.9 ± 0.2	2.2 ± 0.4	2.2 ± 0.4	
Eb (%)	136 ± 16	146 ± 9	283 ± 30	244 ± 34	295 ± 60	299 ± 73	

TABLE 12 — Kinetics of vulcanization, Payne effect, and mechanical properties of the BR compounds filled with nano-CaCO₃.

detail. As an example, results for BR and BR/VMQ compounds filled with N220 are shown in Figure 3.

Kinetics of Vulcanization

The main purpose of measuring the kinetics of vulcanization of a rubber compound is to get an insight into its final step of processing, which is the vulcanization process. The scorch time parameter ($t_{02} = 2\%$ of the torque increase) provides information about the beginning of the vulcanization and as such about the processing safety of a compound, while the vulcanization time ($t_{90} = 90\%$ of the torque increase) shows when the rubber macromolecule cross-

	Samples denotation					
Property	BR-VMQ-CaCO ₃ -5	BR-VMQ- CaCO ₃ -15	BR-VMQ-CaCO ₃ -30			
Kinetics of vulcaniza	tion					
S'_{\min} (dNm)	0.7	0.8	0.8			
$S'_{\rm max}$ (dNm)	9.7	11.2	12.3			
<i>t</i> ₀₂ (min)	3.0	4.6	3.8			
<i>t</i> ₉₀ (min)	7.6	12.9	11.1			
Payne effect						
$\Delta G'$ (kPa)	1.6	15.4	23.7			
G'@20% (kPa)	84.5	90.9	95.7			
Mechanical propertie	s					
Ts (MPa)	1.6 ± 0.2	1.5 ± 0.1	1.7 ± 0.1			
Eb (%)	272 ± 54	206 ± 19	232 ± 25			

TABLE 13 — Kinetics of vulcanization, Payne effect, and mechanical properties of the BR/VMQ compounds filled with nano-CaCO₃.



FIG. 2 — Changes to storage modulus in the function of strain for the BR compounds filled with N220.

linking reaches the final phase. Other important parameters are the minimum (S'_{\min}) and maximum (S'_{\max}) torque values, which characterize the compound viscosity and the cross-link density, respectively.

The addition of fillers often influences the kinetics of vulcanization of rubber compounds. For example, the introduction of carbon black decreases the scorch time of the compounds (Tables 8–13). This effect is known from the literature, and recently it was proved that the CB surface acts catalytically in contact with sulfur-based curing systems [19]. A similar effect is noticed for the studied compounds, for example, the influence of various amounts of N220 addition to BR is shown in Figure 4. It is clear that the addition of only 5 phr of N220 results in a significant reduction of the scorch time. Further addition of 15



FIG. 3 — Changes to storage modulus in the function of strain for the BR and BR/VMQ compounds filled with 30 phr of N220.



FIG. 4 — Kinetics of vulcanization of the BR compounds filled with various amounts of N220.

phr and 30 phr of N220 decreases the scorch time only slightly, showing that even a small dose of the CB can speed up the vulcanization significantly.

A similar effect is observed for the compounds filled with nano-CaCO₃. This strongly suggests that its surface might play a similar role to CB, especially considering the fact that lipoic acid increased the scorch time to a similar level as in the unfilled reference compound. Carboxylic acids are well known coupling or covering agents for CaCO₃ fillers, improving the properties of rubber composites [20]. Lipoic acid is added as a coupling agent that covers the nano-CaCO₃ surface, which might allow the formation of covalent bonds between the filler and rubber. Carboxylic acids are prone to complex formation with the hydrated calcium atoms present on the CaCO₃ surface, while the disulfidic moiety of the lipoic acid is expected to covalently bond with sulfur or carbon-carbon double bond of BR during vulcanization. Additionally, its complexation and presence on the CaCO₃ surface seem to prevent the curatives from catalytic premature decomposition by steric shielding of the surface. A different effect is observed when silica is added to the rubber matrix-a steady increase of the torque without reaching a visible plateau. This effect is called "marching modulus." Its origin is related to strong filler-filler interactions, silica flocculation rate, and filler-rubber coupling rate. Additionally, the reversible adsorption of curatives on the large surface of silica usually results in an increase in scorch time. At the beginning of the vulcanization, the strong filler-filler interactions cause silica flocculation, resulting in a "marching" increase of the modulus until the flocculation rate reaches its highest value. The filler-polymer coupling rate affects the kinetics of vulcanization as well. The slower it is, the higher the "marching" effect. The coupling rate depends not only on the type of silane but also on the sulfur amount that is used for the silane activation [21]. In the current study, the



FIG. 5 — Kinetics of vulcanization of the BR compounds filled with 30 phr of various fillers.

amount of sulfur activating the silane might depend on the specific surface area of the used silica. The higher the specific surface area is, the more sulfur might be adsorbed on it and, as a result, less is needed for the silane activation [22]. Alternatively, sulfur might covalently attach to the disulfide fragments of TESPD, forming polysulfide chains. Also, the CBS accelerator, which exhibits a basic nature, is likely to adsorb on the acidic silica surface, affecting the kinetics of vulcanization. This is visible in a relatively low torque increase of the BR and BR/VMQ compounds containing the highest specific surface area of silica-Ultrasil 9100 GR (Tables 10 and 11). Their torque increase is noticeably lower than for the compounds filled with lower specific surface silicas. This is in contradiction with the highest capability of filler structure formation (filler-filler and filler-rubber interactions) that Ultrasil 9100 GR exhibits. However, it is very much in line with the effect of the curatives adsorption on the Ultrasil 9100 GR surface. The highest specific surface area results in the highest amount of the curatives adsorbed, effectively decreasing vulcanization efficiency. The comparison of the effect of the presence of CB, silica, and nano-CaCO₃ on the kinetics of the vulcanization of the rubber compounds is shown in Figure 5. Moreover, it is clear that the incorporation of CB and silica resulted in a much higher increase in S'_{min} stemming from much higher filler-filler and filler-rubber interaction imposed by these fillers in comparison to nano-CaCO₃.

Considering the fact that CBs play a catalytic role in sulfur vulcanization, one can observe that the kinetics of vulcanization results support the hypothesis that CB locates preferably in one of the rubber phases of BR/VMQ blends, most likely BR. The scorch time of CB-filled BR/VMQ blends is visibly shorter in comparison to BR compounds with the same type and amounts of carbon black.



FIG. 6 — Kinetics of vulcanization of the BR and BR/VMQ compounds—unfilled and filled with 30 phr of N220.

Moreover, the unfilled BR/VMQ compound also exhibits faster vulcanization in comparison to the BR reference. This is probably because silicone rubber is much less likely to take part in sulfur vulcanization due to a much smaller amount of unsaturated carbon–carbon bonds. Therefore, a higher concentration of curatives is used for BR cross-linking. As an example, the kinetics of vulcanization of BR and BR/VMQ compounds filled with 30 phr of N220 is shown in Figure 6. It is also noticeable that the maximum torque (S'_{max}) is higher for BR compounds in comparison to their BR/VMQ counterparts. This suggests that the VMQ is less likely to be sulfur vulcanized. The amount of vinyl groups in the VMQ is relatively low in comparison to the unsaturated BR main chain. This, most likely, results in the formation of rubber blends consisting of a well-cross-linked BR phase and a less-cross-linked or non-cross-linked VMQ phase. To investigate this, further work must be done, for example by investigating the effectiveness of sulfur-curing of the VMQ blends.

Mechanical Properties

The mechanical properties of most synthetic rubbers strongly depend on the reinforcing filler addition due to the weak intramolecular interactions of their macromolecules. Butadiene and silicone rubbers are no exceptions in this matter. Reinforcing fillers improve the tensile strength (Ts) and increase the elongation at break (Eb) of rubber compounds by forming an in-rubber structure based on filler–filler and filler–rubber interactions [23]. A potentially reinforcing filler needs to exhibit a small primary particle and cluster size, a high specific surface area, a high-structure penetrable by rubber molecules, and surface properties promoting filler–filler and filler–rubber interactions. Based on the literature, nano-CaCO₃ seems to be able to provide good reinforcing

properties even though its specific surface area is relatively low in comparison to CBs or silica. Fang et al. studied natural rubber reinforcements with nano-CaCO₃ and obtained promising results [10]. However, in the present study, the nano-CaCO₃ does not provide any reinforcement regardless of whether the lipoic acid was used as a coupling agent or not. This might be explained by the crystalline morphology of nano-CaCO₃ particles, which differs significantly from amorphous silica clusters or turbostratic CB aggregates, and possibly are much less effective in forming an in-rubber structure. Also, the specific surface area of the used nano-CaCO₃ is most likely low (in the range of $30 \text{ m}^2/\text{g}$), which has a significant impact on the reinforcing potential of the nano-CaCO₃. In such a case, the maximum amount of 30 phr of the filler addition was not sufficient to obtain a reinforcing effect. Additionally, if the reinforcing potential of the used nano-CaCO₃ is too low in general, its higher addition level would only worsen the mechanical properties of rubber. For the CB-filled and silica-filled compounds, 30 phr of the filler addition was sufficient to achieve satisfactory reinforcement exhibited by good mechanical properties and a high value of Payne effect for both BR compounds and VMQ/BR blends. Interestingly, CBfilled BR/VMO blends exhibit better mechanical properties in comparison to BR compounds. Usually, a greater homogeneity of a rubber compound results in better mechanical properties. Thus, one might expect that the potentially inhomogeneous distribution of filler in the BR/VMQ blends would result in worse mechanical properties. However, a possible explanation of this phenomenon might be related to the improved filler-filler interactions resulting from higher CB concentration in the BR phase, as is shown by the Payne effect results (Figure 3). Alternatively, CB might accumulate in the BR/VMQ interphase, as is reported by the literature for immiscible polymer blends [18], and form a strong network of aggregates densely packed in the interphase region, that provides the reinforcement. In such a case, the filler interacts with both rubber phases, assuring their contribution to the mechanical properties. This also explains the high Payne effect for the blends. Exemplary stress-strain plots of the compounds filled with N220 are shown in Figure 7.

A clearly different tendency is observed for the silica-filled compounds. Even though the Payne effect results show a similar pattern to the CB-filled compounds, the mechanical properties of silica-filled BR/VMQ blends are worse than the BR compounds. This can be explained by poor or no coupling between silica and silicone rubber, which have a considerably smaller amount of unsaturated bonds, reactive with the silane coupling agent, than butadiene rubber. And if the silica clusters are preferably located in the BR/VMQ interphase they reinforce mainly the BR phase by the strong covalent links provided by the silane, while their interaction with VMQ is very weak due to the hydrophobation of the silica surface. Alternatively, this can be a morphological effect. The size of the VMQ domains in the blends filled with CB or silica may vary. In such a case, the bigger the VMQ domains are, the



FIG. 7 — Tensile properties of the BR and BR/VMQ compounds—unfilled and filled with 30 phr of N220.

poorer the mechanical properties of the compound. It cannot be excluded that the silica-filled blends contain bigger VMQ domains, resulting in a lack of noticeable reinforcement in comparison to the BR compounds. Also, this would result in poorer mechanical properties as observed. Exemplary stress–strain plots of the compounds filled with Ultrasil9100 are shown in Figure 8.

Differential Scanning Calorimetry

DSC is a useful tool in polymer engineering, giving information about the glass transition temperature of rubber [24]. Also, crystallization and melting temperatures, and the amount of the crystalline phase for the semi-crystalline rubbers are measured using DSC. The DSC technique allows also for studying



FIG. 8 — Tensile properties of the BR and BR/VMQ compounds—unfilled and filled with 30 phr of Ultrasil 9100.



FIG. 9 — DSC plots of the unfilled BR and BR/VMQ compounds.

rubber miscibility by investigating changes in the rubber T_g . For non-miscible blends, there is no shift in the rubber T_g , while ideally miscible rubbers merge their T_g . For example, Yehia et al. investigated the miscibility of BR/NR, NR/NBR, and CR/NBR blends using DSC [25].

In the current study, the DSC technique was used to investigate the BR/ VMQ blending (Figure 9) and the effect of the incorporation of the fillers on the rubber compounds (Figures 10 and 11).

The DSC analysis of the BR and BR/VMQ revealed that both rubbers are semi-crystalline. Crystallization of VMQ occurs around -95 °C, and melting of the crystalline phase around -40 °C, while crystallization of BR takes place around -60 °C, and melting of the crystalline phase around -20 °C. The glass transition temperature of BR shifts very slightly after blending with VMQ toward the T_g of VMQ. This is most likely an effect of the limited covulcanization of the BR and VMQ macromolecules because silicone rubber is not miscible with organic rubbers thermodynamically. Only a chemical trigger is able to improve the silicone-organic rubbers compatibility. The VMQ grade used in this study contains 1 mol.% of methyl-vinyl mers that can take part in sulfur vulcanization [26].

The addition of the fillers results in a decrease in the crystallization temperature of BR and an increase in the amount of the crystalline phase. This is evidenced by the shift of the crystallization peak onset to lower temperatures and by higher melting peaks, respectively. This is observed for all the fillers regardless of their type or content. It is a common phenomenon that the



FIG. 10 — DSC plots of the reference and filled BR compounds.

presence of additives or impurities enhances polymer crystallization because they act as nucleating agents initiating the growth of crystallites. For example, it was reported that the impurities present in natural rubber nucleate its crystallization [27]. Interestingly, adding the fillers to BR/VMQ blends resulted in the nucleation of BR crystallization but also a very significant decrease in VMQ crystallization (Figure 11). This is most likely an effect of the improved dispersion of the VMQ phase within the BR phase by increased shear forces present during mixing, which were caused by the filler addition. As a result, the VMQ chains are separated from each other and cannot form domains big enough for crystallization. The significant effect of the fillers on BR crystallization suggests their preferential location in the BR phase or BR/ VMQ interphase. Usually, the introduction of fillers into rubber blends does not shift their glass transition temperature. However, considering the unusual combination of silicone and butadiene rubber in the blend, it couldn't be excluded. The obtained results confirmed that the presence of fillers has no visible effect on the glass transition temperature of the rubber compounds. This



FIG. 11 — DSC plots of the reference and filled BR/VMQ compounds.

is a very important finding from the point of view of the practical use of the compounds in the Mars environment. Assuring good low-temperature elasticity is one of the most important challenges in designing rubber materials for the Martian environment. The performed DSC analysis confirmed that the application of CB, silica, or nano-CaCO₃ doesn't affect the T_g value of BR and VMQ.

Dynamic-Mechanical Analysis

The dynamic performance of rubber is one of its most important features because it exploits the unique visco-elastic behavior, which provides elasticity and damping properties. Analyzing the dynamic behavior of rubber in the function of temperature gives information about the rubber's glass transition temperature and elastic (storage modulus, E') and damping (loss modulus, E'') properties. The T_g values measured by DMA differ noticeably from the values measured by DSC because of the different principles of measurement. In the DMA test, the rubber sample is exposed to a frequently changing force field,



FIG. 12 — DMA plots of the unfilled BR and BR/VMQ compounds.

and its response is measured as a function of temperature, while in the DSC test, the changes in thermal capacity of the samples are measured as a function of temperature. It is known from the literature that the results obtained from these two techniques usually vary without either technique showing a clear tendency to provide higher or lower values than the other [28]. Therefore, both techniques were used to double-check whether the addition of the fillers would affect the T_g of the BR/VMQ blends. Rubber materials are designed to be used above their T_g in the dynamic region called the *rubbery plateau*, in which its elastic and damping properties are dominating due to the free segmental movement of rubber macromolecules. The complex modulus (E^*) is a vector sum of the storage and loss moduli and is often used to analyze the dynamic-mechanical properties of rubber. The changes in E^* in the function of temperature of the unfilled BR and BR/VMQ compounds are shown in Figure 12.

The significant drop in the E^* value at around -90 °C marks the BR glass transition temperature that determines the dynamic behavior of the BR compounds but also of the BR/VMQ blends, as butadiene rubber is the continuous phase. Interestingly, BR/VMQ exhibits a higher value of E^* , even though most of the VMQ chains are probably non-cross-linked and the other tests imply that it behaves like a plasticizer (Figures 1, 3, 6, 7, and 8). This might be explained by the additional crystalline fraction formed by the silicone rubber that increases the value of the modulus. Both compounds exhibit a significant increase in E^* value in the temperature range between BR crystallization and melting of the crystalline phase, clearly stemming from the crystalline phase contribution to the modulus. The effect of the addition of the fillers on the rubber is shown in Figure 13.

Like the DSC results, DMA measurements also confirm that the addition of the fillers does not change the glass transition temperature of the rubber compounds. Various studies show that in some cases incorporation of a reinforcing filler might increase the T_g of a compound noticeably. For example,

recently Bandyopadhyaya et al. reported that the addition of N330 increases the T_g of natural rubber-based compounds significantly [29]. The most visible change is the increase of E^* after the fillers' incorporation and the disappearance of the modulus drop between the T_g and the crystallization temperature caused by the nucleating effect exhibited by the fillers. The crystallization temperature decreases close to the value of the glass transition of BR. Therefore, the complex modulus, which is dropping as a consequence of the initiation of segmental mobility of the macromolecules at T_g , rises again because of the crystalline phase formation. The addition of the fillers resulted in a significant increase of the E^* modulus regardless of the filler type or grade. The E^* increase was the highest for the most reinforcing grades of CB (N220) or silica (Ultrasil 9100), which is in line with the Payne effect and mechanical properties results.

Conclusions

One of the most important challenges in designing rubber for Mars missions is assuring its possibly low glass transition temperature that ensures elasticity at Mars's low temperatures. Development of high-performance rubber is impossible without using reinforcing fillers, which in some cases are reported to increase the glass transition temperature of rubber compounds. Therefore, the aim of this work was to investigate the effect of the most effective rubber fillers on BR compounds and BR/VMQ blends, which are the most promising matrices for designing rubber for Mars applications because of their low glass transition temperature. The BR compounds are used as internal references to investigate the performance of the unusual BR/VMQ blends. VMQ is thermodynamically non-miscible with organic rubbers like BR. Also, the common curing techniques of VMQ and BR are completely different. However, to achieve new low-temperature performance, a blending of these two types of rubber seems to be promising, because it can bring a synergistic effect. VMQ exhibits lower T_g and better UV resistance than BR, while BR has better mechanical properties and wear resistance than VMQ. Also, it was previously shown that BR can be effectively homogenized with VMQ on a micro-scale by chemical coupling [30,31] or by the addition of a reinforcing filler [32]. Both DSC and DMA techniques confirmed that the addition of up to 30 phr of the fillers does not increase the T_g of the compounds. However, a satisfactory reinforcing effect is observed only for the vulcanizates filled with at least 30 phr of the reinforcing CBs or silicas. The BR/VMQ blends filled with CBs exhibit better mechanical properties than their BR counterparts even though the polymers are incompatible. This may be explained by the preferential location of the CB aggregates in the BR phase or BR/VMQ interphase resulting in formation of a strong network because of the short distance between the CB aggregates. Using



FIG. 13 — DMA plots of the BR compounds filled with (a) CB, (c) silica, and (e) nano-CaCO₃, and BR/VMQ blends filled with (b) CB, (d) silica, and (f) nano-CaCO₃.



FIG. 13 — Continued.

silica as a reinforcing filler results in worse mechanical properties of the BR/ VMQ vulcanizates compared to the BR compounds. This is because of the limited ability of filler–silicone rubber coupling by the current state-of-the-art silane, which is based on the formation of sulfidic links. Also, the size of VMQ domains inside the BR matrix may vary for silica and CB compounds, leading to improved or worsened mechanical properties. The highest reinforcing effect is noticed for the N220 CB and Ultrasil 9100 silica, which both have the highest specific surface areas from their filler group within this study. As a reinforcing filler, the N220 grade CB provides the best properties; however, considering the potential of in situ silica production on Mars development of a new silica-VMQ coupling system could make the use of reinforcing silica more prospective. Alternatively, a blend of CB and silica also can be considered a promising system for further study. The nano-CaCO₃ does not provide any noticeable reinforcing effects within the applied amounts. The biggest disadvantage of the designed compounds might be their crystallization and melting in the daily temperature range of Mars. This effectively excludes these compounds from any sealing application. Macroscopically, crystallization results in a shrinkage of the material and its stiffening, which might have catastrophic results if such a compound is used as a seal, as was tragically proven by the Challenger disaster [33]. In that case, the fillers' addition effectively diminished the VMQ crystallization. In this light, it is recommendable that for future work a noncrystallizable grade of BR should be considered. In conclusion, further development of BR/VMQ blends seems to be a promising pathway for designing functional rubber elements for Mars missions.

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