

## Some Properties of Composites Based on Vulcanized Liquid Polybutadiene Matrix and Inorganic Particulate Fillers

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**ABSTRACT:** This study is primarily focused on the possibility to use a sulfur vulcanized low-molecular weight polybutadiene with isocyanate end groups in the main chain as a matrix for composite materials reinforced with common inorganic particulate fillers (calcium carbonate, titanium dioxide, titanium dioxide modified with zinc, respectively). The isocyanate groups were used for a preliminary crosslinking of the oligomeric polybutadiene with glycerol as a three-functional crosslinker. The prepared polybutadiene-based polyurethane gel was subsequently vulcanized with sulfur. It has been shown that the vulcanized liquid polybutadiene could be successfully applied as the matrix for composite materials with inorganic filler. The resulting composite materials exhibited enhanced mechanical properties (tensile strength, flexural strength, hardness) and retain a high chemical resistance against hydrolysis and aqueous solutions of chemicals. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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### INTRODUCTION

Composite materials comprising polymeric matrix and fibrous or particulate fillers represent an important group of widely used sophisticated materials. The addition of fillers into a polymeric matrix affects processing characteristics and should achieve improvements in technological properties and reduction in cost as well. To satisfy these objectives, the filler should accomplish numerous requirements. For the concept of reinforcement, the filler must improve compound properties such as tensile strength or abrasion resistance.<sup>1,2</sup> Currently, various inorganic materials such as calcium carbonate, mica, and so forth are frequently used as reinforcing particulate fillers in composite materials and their positive effect on mechanical properties of resulting composites is well documented in the literature.<sup>3–8</sup>

Highly promising materials applicable as polymeric matrices of composite materials are the crosslinked elastomers based on low-molecular weight polybutadiene rubbers. Their hydrocarbon chains are very resistant against hydrolysis, acids, alkalies, and aqueous salt solutions. Polymeric binders and matrices based on low-molecular weight polybutadienes have been successfully used in building industry, electric engineering, anticorrosion technologies,<sup>9</sup> and so forth. They possess advantageous elasticity, excellent low-temperature properties, low permeability for water vapors, capability of filling with pigments and fillers,

good adhesion to various substrates, particularly metals, excellent electro-insulating properties and very good thermal insulation properties.<sup>10</sup>

Different liquid polybutadiene commercial products are available on market, the telechelic ones playing the most important role. Polybutadienes terminated with isocyanate groups enable two different principles of crosslinking, either reaction of isocyanate groups with polyols and/or vulcanization with sulfur. It is well known that vulcanization process in the presence of accelerators takes place on allylic carbon atoms.<sup>11</sup> In this case, the carbon atom within the polymeric backbone is activated by the vinyl groups which are present as a result of 1,2-addition of butadiene units. Actually, the content of more than 50% of 1,2-vinyl groups in the microstructure is usual. This activation enables effective crosslinking with sulfur. Nevertheless, it becomes evident from the literature survey that no work has been carried out on sulfur-vulcanized liquid polybutadienes applied as matrixes in composite materials.

In the previous article,<sup>12</sup> we reported on the results of a study based on isocyanate precrosslinked and additionally with sulfur-vulcanized polybutadiene/glass fiber composites. Being vulcanized with sulfur, the polybutadiene matrix was found to possess enhanced mechanical and flexural properties and retain excellent electroinsulating characteristics. Accordingly, we decided to

**Table I.** Typical Properties of the Polybutadiene KRASOL LBD 3000<sup>a</sup>

Property	Numeric Value
$\overline{M}_n$ (g/mol)	3200–3800
Polydispersity index $\overline{M}_w/\overline{M}_n$	ca. 1.3
Functional group concentration (mmol/g)	0.65–0.75
Amount of toluene diisocyanate (wt. %)	0.8–1.53
Microstructure 1,4- <i>cis</i> (%)	ca. 15
Microstructure 1,4- <i>trans</i> (%)	ca. 25
Microstructure 1,2- (vinyl) (%)	ca. 60
Specific gravity, 25°C (g/cm <sup>3</sup> )	0.9

<sup>a</sup>Data given by suppliers.

continue our research work on isocyanate precrosslinked and additionally sulfur-vulcanized liquid polybutadiene-based composites. This research work is mainly focused on the effects of the addition of commonly used particulate fillers on mechanical properties and chemical resistance of liquid polybutadiene-based composites.

## EXPERIMENTAL

### Materials

All the composite materials were made of the low-molecular weight polybutadiene KRASOL LBD 3000 (Synthos Kralupy, Czech Republic) bearing isocyanate groups at the ends of the polymeric chain. This kind of polybutadiene is a “prepolymer,” predominantly developed for the synthesis of polybutadiene-based polyurethanes which can be applied as casting systems, for example, for sealants of coating compositions, binders, adhesives, foamed materials, and so forth. Typical properties of the polybutadiene KRASOL LBD 3000 are listed in Table I. MgO (Merck) was used as an activator and tetramethylthiuram disulfide (TMTD, Sigma-Aldrich) was used as an accelerator of the vulcanization reaction. Dibutyltin dilaurate (DBTL, Sigma-Aldrich) was used as a catalyst of the isocyanate reaction. Glycerol and sulfur (Lach-Ner, Czech Republic) were used as crosslinking agents.

Calcium carbonate OMYACARB 4-LU (Omya, Czech Republic), titanium dioxide PRETIOX RGX and titanium dioxide PRETIOX RD-55 (Precolor, Czech Republic) were used as the reinforcing particulate fillers in this study. The basic parameters of the investigated fillers are summarized in Table II. The choice of the investigated three fillers was driven from the point of view of their commercial availability and nature of surface treatment. The filler surface treatment may affect adhesive interfacial forces between filler particles and polymer matrix, thus leading to differences in mechanical and chemical properties of resulting materials. As titanium dioxide has been supplied either hydrophobic surface treated (PRETIOX RGX) or hydrophilic surface treated (PRETIOX RD-55), we used these two different materials. Calcium carbonate as a widely used and nonexpensive filler was chosen for comparison as a representative without surface treatment.

### Preparation of Composites

On the basis of results reported in the previous research study,<sup>12</sup> all the composite materials were based on the polybutadiene

matrix containing 20 phr of sulfur. Composite materials comprising variable content (0–40 wt %) of calcium carbonate OMYACARB 4-LU (hereinafter CaCO<sub>3</sub>), titanium dioxide PRETIOX RGX (hereinafter TiO<sub>2</sub> RGX), and titanium dioxide PRETIOX RD-55 (hereinafter TiO<sub>2</sub> RD-55), respectively, were prepared. All the starting materials (see Table III) except the catalyst DBTL were mixed with the polybutadiene KRASOL LBD 3000 for 15 min at 50°C using a hook-shaped mixer. To avoid the gelation, DBTL in the form of 5% solution in toluene was added after the proper homogenization. The reaction mixture was then poured into a hot mould and heated at 90°C for 45 min. At these conditions, the isocyanate groups present at the end of the polybutadiene chain reacted with glycerol to form urethane crosslinks. Then, the mould was placed into the vulcanizing press P 11-E (Kovopodnik Vlašim, Czech Republic) at a pressure 3 MPa and cured at 155°C for 4 h. During this period, the vulcanization reaction between unsaturated polybutadiene chains and sulfur took place.

### Evaluation of Composites

After aging at room temperature for 1 month, the resulting composite materials comprising variable amount of reinforcement made of CaCO<sub>3</sub>, TiO<sub>2</sub> RGX, and TiO<sub>2</sub> RD-55, respectively, were evaluated for their mechanical properties (tension, flexure, Charpy impact strength, and Brinell hardness), heat-resistant performance (Vicat temperature) and extractable portion in chloroform. The chemical resistance of composites containing 20 wt % of different reinforcing fillers was evaluated according to weight, flexural, and hardness changes of tested samples immersed at room temperature for 1 month in distilled water, 30% H<sub>2</sub>SO<sub>4</sub>, 40% NaOH, and 50% ethanol, respectively. All the results were compared with those of the neat matrix.

Tensile strength values of composites were determined using the MTS-4/M universal testing machine (Sintech—MTS Systems Corporation) at a crosshead speed of 5 mm/min. Tests were performed according to ISO 527. The sample size used for the tensile tests was 150 × 10 × 4 mm<sup>3</sup>. Flexural properties were evaluated using a three-point bending test according to ISO 178 using the MTS-4/M universal testing machine at a crosshead speed of 2 mm/min. For the flexure tests, the sample dimension was 80 × 10 × 4 mm<sup>3</sup>. Impact strength measurements were

**Table II.** Technical Parameters of Particulate Fillers Calcium Carbonate OMYACARB 4-LU, Titanium Dioxide PRETIOX RGX, and Titanium Dioxide PRETIOX RD-55<sup>a</sup>

Property	Type of Filler		
	CaCO <sub>3</sub>	TiO <sub>2</sub> RGX	TiO <sub>2</sub> RD-55
CaCO <sub>3</sub> or TiO <sub>2</sub> content (%)	98	98	92
Inorganic coating	None	Alumina	Alumina, zinc
Organic treatment	None	Hydrophobic	Hydrophilic
Particle size (μm)	3.5	0.34	0.42
Specific gravity (g/cm <sup>3</sup> )	2.7	4.2	4.0

<sup>a</sup>Data given by suppliers.

**Table III.** Composition of Tested Samples

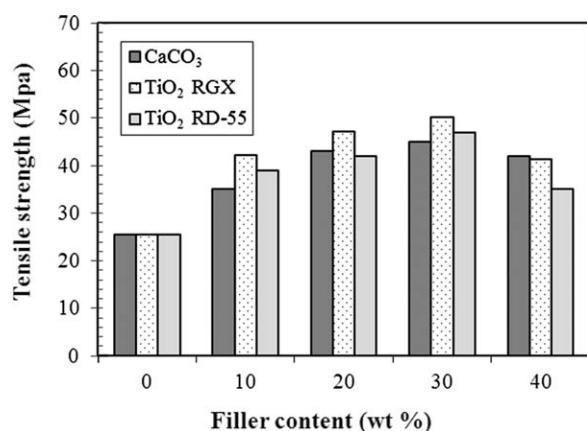
Filler content (wt %)	Filler (g)	LBD (g)	Glycerol (g)	Starting material			
				Sulfur (g)	TMTD (g)	MgO (g)	DBTL soln. (drops)
0	0	79.78	2.03	15.95	1.59	0.80	8
CaCO <sub>3</sub>							
10	10.70	77.00	1.53	15.34	1.53	0.77	10
20	23.10	73.80	1.47	14.76	1.48	0.74	11
30	37.50	69.96	1.39	13.99	1.40	0.70	12
40	54.60	65.40	1.30	13.10	1.30	0.66	13
TiO <sub>2</sub> RGX							
10	10.90	77.90	1.55	15.58	1.56	0.78	8
20	23.70	75.60	1.51	15.12	1.51	0.76	9
30	39.20	73.00	1.46	14.60	1.46	0.73	10
40	58.30	69.80	1.39	13.94	1.39	0.70	11
TiO <sub>2</sub> RD-55							
10	10.90	77.90	1.55	15.58	1.56	0.78	8
20	23.70	75.60	1.51	15.12	1.51	0.76	9
30	39.20	73.00	1.46	14.60	1.46	0.73	10
40	58.30	69.80	1.39	13.94	1.39	0.70	11

performed according to ISO 179 using the VEB 400/69/40 testing machine (Werkstoffprüfmaschinen Leipzig, Germany). The sample size used for the test was  $50 \times 6 \times 4 \text{ mm}^3$ . Hardness testing was performed according to ISO 2039-1 by the VEB 300/22 tester (Werkstoffprüfmaschinen Leipzig, Germany). All the measurements of mechanical properties and chemical resistance were performed 10 times for each type of composite at room temperature to check the reproducibility. The measurements of heat-resistant performance were performed according to ISO 306. The HDT3 VICAT (CEAST, Italy) was used to measure the Vicat temperature. The sample size used for the test was  $10 \times 10 \times 4 \text{ mm}^3$ . The constant heating rate and load were  $50^\circ\text{C/h}$  and 0.1 MPa, respectively. The testing of the extractable portion was evaluated according to ISO 175. Around 0.5 g of the finely grated sample was allowed to swell in 50 mL of chloroform for 20 min at room temperature. The solution of

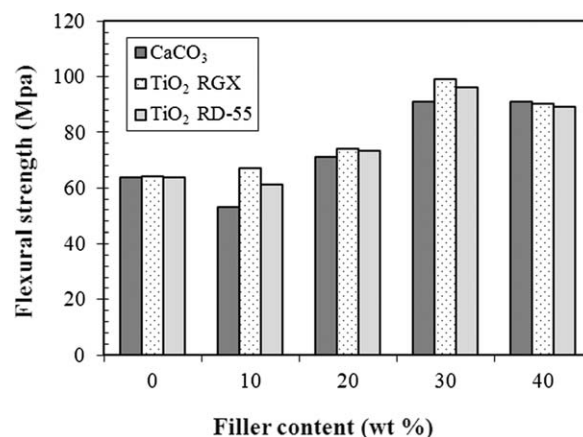
low-molecular weight portion was filtered, dried, and weighted. All the measurements of heat-resistant performance and extractable portion were performed five times for each type of composite to check the reproducibility.

## RESULTS AND DISCUSSION

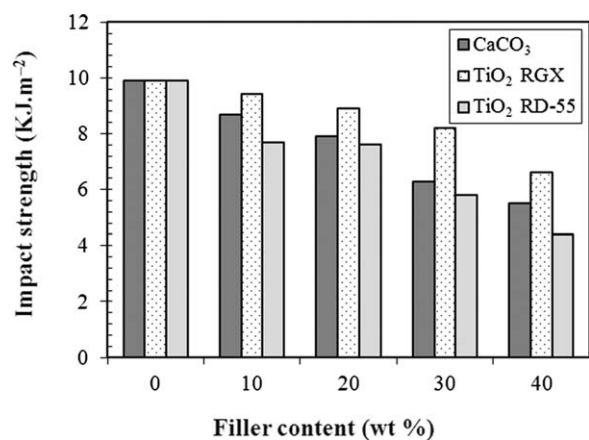
Figures 1–4 demonstrate the mechanical properties of liquid polybutadiene-based composite materials varying in the type and content of inorganic particulate filler. It was found that the tensile and flexural properties of composites were improved by the addition of all kinds of tested fillers, in contrast to the neat matrix (see Figures 1 and 2). It was shown as well that the tensile and flexural strength values grew until the content of filler reached 30 wt %, whereon a slight drop in tested properties occurred at the filler content 40 wt %. Further, when comparing



**Figure 1.** Dependence of the tensile strength of composites on the filler content, for different inorganic particulate fillers.



**Figure 2.** Dependence of the flexural strength of composites on the filler content, for different inorganic particulate fillers.

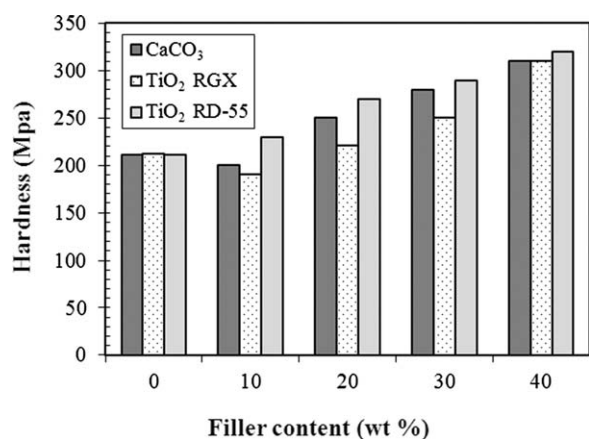


**Figure 3.** Dependence of the Charpy impact strength of composites on the filler content, for different inorganic particulate fillers.

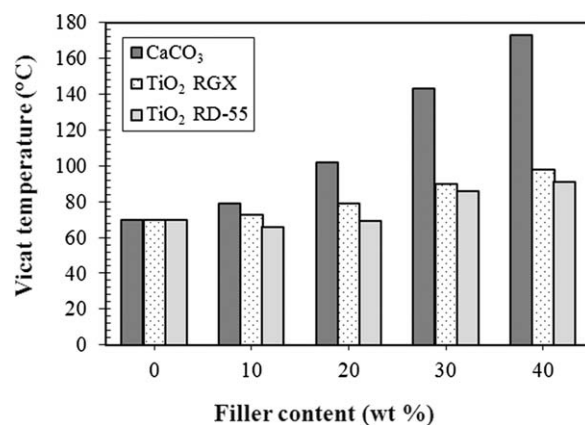
the tensile and flexural results for three inorganic fillers, namely CaCO<sub>3</sub>, TiO<sub>2</sub> RGX, and TiO<sub>2</sub> RD-55, the filler TiO<sub>2</sub> RGX with the hydrophobic surface treatment was found to improve the tensile and flexural strength most significantly. The reason of this fact may be based on the stronger interfacial adhesive forces between the nonpolar polymeric matrix and the hydrophobic surface-treated filler particles.

A decrease in impact strength values of composites with the increasing filler loading was observed when comparing the values of reinforced composites with neat matrix (see Figure 3). This result indicates cohesive composite materials possessing filler particles regularly distributed inside the polymeric matrix and strong adhesive interfacial forces between the polymer and inorganic fillers. When comparing the results of all types of inorganic fillers, the hydrophobic surface-treated filler TiO<sub>2</sub> RGX was found to deteriorate the impact strength of composites the least, which indicated the best adhesion between the TiO<sub>2</sub> RGX particles and the liquid polybutadiene-based matrix, as already mentioned above.

The effect of the filler content on the Brinell hardness of composites illustrates Figure 4. It can be observed that the hardness



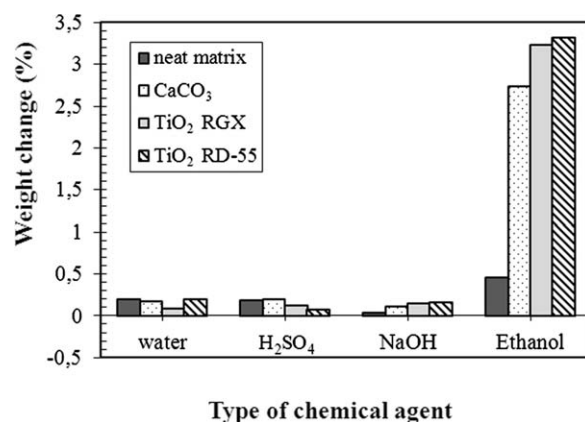
**Figure 4.** Dependence of the Brinell hardness (straining time 60s) of composites on the filler content, for different inorganic particulate fillers.



**Figure 5.** Dependence of the heat-resistant performance (expressed by the Vicat temperature) of composites on the filler content, for different inorganic particulate fillers.

values were rising with the increasing filler content and the composites comprising particulate fillers in the content of 20–40 wt % exhibited higher values of hardness in comparison with the neat matrix. The most significant effect on hardness improvement was observed in the case of the hydrophilic surface treated filler TiO<sub>2</sub> RD-55.

The results of the heat-resistant performance of composites varying in the amount and type of reinforcing fillers are represented in Figure 5. Except the case of CaCO<sub>3</sub> reinforcement, it can be stated that both the hydrophobic surface treated filler TiO<sub>2</sub> RGX, and the hydrophilic surface treated filler TiO<sub>2</sub> RD-55 affected the heat-resistance of composite materials negligibly, only a slight enhancement of Vicat temperature can be observed with the increasing filler content. On the contrary, the incorporation of CaCO<sub>3</sub> filler particles led to a significant elevation of Vicat temperature with the raising filler loading. This phenomenon may be explained by the difference in the filler particle size (see Table II). When the temperature exceeds the glass transition temperature of the polymeric matrix (61.3°C),<sup>11</sup> the CaCO<sub>3</sub> filler particles having the mean particle size 3.5 μm are believed to act as a protective mechanical barrier against the



**Figure 6.** Effect of 1 month exposure in chemical agents on the weight change of composites comprising 0 and 20 wt % of CaCO<sub>3</sub>, TiO<sub>2</sub> RGX, and TiO<sub>2</sub> RD-55, respectively.

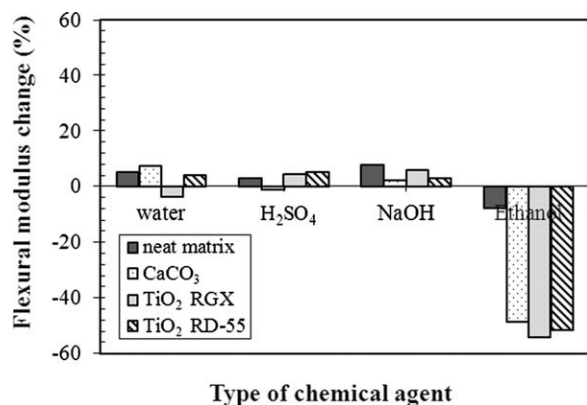


penetration of a Vicat tip more effectively than the TiO<sub>2</sub> RGX or TiO<sub>2</sub> RD-55 filler particles having the mean particle size around 0.3–0.4 μm. Accordingly, this heat-resistant effect of CaCO<sub>3</sub> reinforcement is more evident at higher loading.

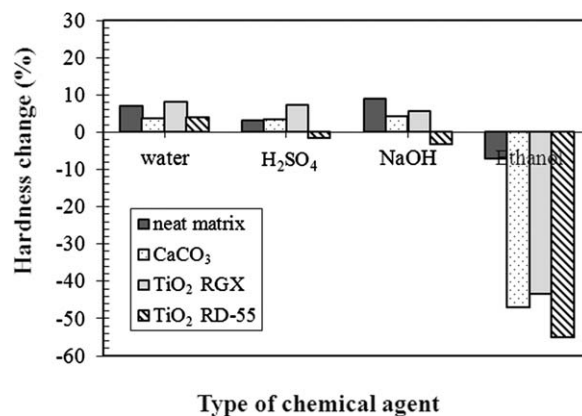
The neat matrix and all the composites varying in the filler type and loading were tested from the point of view of the extractable portion. It was found that neither low-molecular weight soluble molecules nor inorganic filler particles were extracted from all the investigated samples, which indicates composite materials composed of a completely crosslinked polymeric matrix and sufficiently interfacially bonded filler particles.

The composites comprising all the investigated kinds of particulate fillers in the amount of 20 wt % were tested from the point of view of the chemical resistance (see Figures 1–4). The results of chemical resistance measurements were expressed in terms of the weight, flexural, and hardness changes of tested samples immersed in distilled water, 30% H<sub>2</sub>SO<sub>4</sub>, 40% NaOH, and 50% ethanol, respectively, at room temperature for 1 month. Figure 6 demonstrates that only a negligible increase in weight was found in the case of composite samples after immersion in water, 30% H<sub>2</sub>SO<sub>4</sub> and 40% NaOH. The weight elevation was probably related only to the amount of the chemical agent adsorbed on the surface of tested samples. Any significant diffusion and absorption of the chemical agent was not believed to occur. On the contrary, a considerable weight change indicating diffusion and absorption of a chemical agent was determined in the case of ethanol treatment. The composites comprising all kinds of tested fillers exhibited enhanced ethanol absorption in comparison with the neat matrix.

The results of weight change measurements are well correlated to the results of flexural modulus change and hardness change measurements (see Figures 7 and 8). No remarkable improvement or deterioration of flexural modulus or hardness values were found after 1-month exposure of all the tested composite samples and the neat matrix in distilled water, 30% H<sub>2</sub>SO<sub>4</sub>, 40% NaOH, whereas a sharp drop of both the flexural modulus and hardness values occurred after the exposure in 50% ethanol, particularly in the case of all the filled composites. This phe-



**Figure 7.** Effect of 1 month exposure in chemical agents on the flexural modulus change of composites comprising 0 and 20 wt % of CaCO<sub>3</sub>, TiO<sub>2</sub> RGX, and TiO<sub>2</sub> RD-55, respectively.



**Figure 8.** Effect of 1 month exposure in various chemical agents on the Brinell hardness (straining time 60 s) change of composites comprising 0 and 20 wt % of CaCO<sub>3</sub>, TiO<sub>2</sub> RGX, and TiO<sub>2</sub> RD-55, respectively.

nomenon was apparently caused by ethanol entrapped inside the material acting as a plasticizer.

The mechanical properties of the resulting polybutadiene-based composites reinforced with inorganic particulate fillers were compared with those of composites with inorganic particulate reinforcement (titanium dioxide, graphite, glass beads, silica, etc.) and matrices based on polyurethane, epoxide, unsaturated polyester, and vinyl ester resins.<sup>13–17</sup> The comparison has shown that the composites described in this research article exhibited similar mechanical properties as the aforementioned ones, which presents the isocyanate precrosslinked and additionally sulfur vulcanized polybutadiene as a new promising alternative among commonly used polymeric matrixes for composites with inorganic particulate filler reinforcement.

## CONCLUSIONS

The aim of this work was to investigate a low-molecular weight polybutadiene bearing isocyanate end groups as a matrix for composite materials reinforced with commonly used inorganic particulate fillers, namely calcium carbonate, hydrophobic surface treated titanium dioxide, and zinc-modified hydrophilic surface treated titanium dioxide. It has been shown that the sulfur-vulcanized liquid polybutadiene could be the matrix for composite materials with inorganic filler reinforcement. The resulting composite materials were found to exhibit enhanced mechanical properties. The tensile and flexural properties of composites were improved by the addition of all kinds of tested fillers, whereas a decrease in impact strength was observed only at higher filler loading. These results indicate cohesive composite materials possessing regularly distributed filler particles and strong adhesive interfacial forces between the polymer and inorganic fillers.

Moreover, the resulting composite materials were found to retain a high chemical resistance against hydrolysis and aqueous solutions of chemicals. No remarkable improvement or deterioration of flexural modulus or hardness values were found after 1 month exposure of all the tested composite samples and the neat matrix in distilled water, 30% H<sub>2</sub>SO<sub>4</sub>, 40% NaOH, which

proves no significant diffusion and absorption of the investigated chemical agents. A steep decrease of both the flexural modulus and hardness values occurred after the exposure in 50% ethanol, particularly in the case of all the filled composites. This behavior was related to the plasticizing effect of ethanol diffused and entrapped inside.

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