Sulphur-Vulcanized Polybutadiene as a Matrix in Glass Fiber-Reinforced Composite Materials

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ABSTRACT: The basic material used in this work was a low-molecular-weight polybutadiene with isocyanate endgroups in the main chain. The isocyanate groups were used for crosslinking of the oligomeric polybutadiene with glycerol as a three-functional crosslinker. The prepared polybutadiene-based polyurethane gel was subsequently vulcanized with sulphur. The effect of sulphur content on mechanical and electrical properties of resulting materials was investigated with the aim to find an optimum matrix composition for the preparation of composite materials. Several types of glass fiber fabric reinforcement differing in fabric weight and fabric ply thickness were tested. Mechanical properties of composites based on the optimum matrix composition and different types of glass fibers were measured and compared. Being vulcanized with sulphur, the polybutadiene was found to possess improved mechanical properties and retain an excellent electroinsulating character. Moreover, the sulphur-vulcanized polybutadiene was proved good as a matrix for the preparation of glass fiber-reinforced composite materials having enhanced tensile and flexural properties. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 3446–3452, 2011

Key words: polymeric composites; glass fiber reinforcement; polybutadiene; sulphur vulcanization; isocyanate crosslinking

INTRODUCTION

Polybutadienes are prepared from 1,3-butadiene using different initiating and catalytic systems as they are radical, anionic, and Ziegler-Natta initiating systems. This results in a variety of molecular architectures and a wide range of molecular weights. Differences in microstructure (e.g., *cis*-1,4 and *trans*-1,4 isomerism, vinyl groups content, and chain branching) determine the properties of polybutadienes. Higher molecular weight products are solids, whereas low molecular polybutadienes are liquids. Liquid polybutadienes frequently possess various terminal groups (hydroxyl, carboxyl, isocyanate, etc.), which serve for crosslinking and substantially affect their properties. Polymeric binders and matrixes based on liquid polybutadienes are useful in various applications, such as building industry, electric engineering, anticorrosion technologies, and so forth. They have advantageous elasticity, excellent low-temperature properties, resistance against hydrolysis, low permeability for water vapors, perfect resistance against aqueous solutions of chemicals, possibility of filling with pigments and fillers, good adhesion to various substrates, particularly metals, excellent electroinsulating properties, and very good thermal insulation properties.[1]

Composite materials created by combining two ore more components achieve properties, which could not be attained with the separate components. Generally, reinforcing fillers have a positive influence on mechanical properties[2–5] and reduce the cost of final products.[6] Currently, various inorganic materials such as talc, clay, calcium carbonate, mica, and glass fiber are frequently utilized as reinforcing fillers in composite materials.[7–10] Approximately 95% of composites used today are fabricated from glass fibers.[11] Properties of a composite material depend on the properties of its constituent parts, especially on the interaction of interfaces between the reinforcement and a matrix. The shape, size, surface activity, and volume fraction of any filler will influence the final composite properties.[12,13]

In this study, we investigated a possibility to use a sulphur-vulcanized polybutadiene as a matrix for composite materials. An optimum matrix composition in terms of mechanical and electroinsulating properties has been searched and, subsequently, mechanical properties of glass fiber/polybutadiene composites were evaluated by tensile and flexural tests.

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TABLE I
Typical Properties of the Polybutadiene KRASOL LBD 3000[a]

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-*cis* (%)	ca. 15
Microstructure 1,4-*trans* (%)	ca. 25
Microstructure 1,2- (vinyl) (%)	ca. 60
Specific weight, 25°C (g/cm^3)	0.9

[a] Data given by suppliers.

TABLE II
Technical Parameters of Glass Fibre Grid-Lattice Fabrics V240, V301, and V500[a]

	Type of glass fibre fabric		
Property	V240	V301	V500
Length weight of material used (tex)	272	408	680
Fabric weight (g/m^2)	240	301	500
Thickness of a fabric ply (mm)	0.30	0.36	0.57

[a] Data given by suppliers.

EXPERIMENTAL

Materials

The basic material used in this research work was the liquid polybutadiene KRASOL LBD 3000 (Synthos Kralupy, Czech Republic). This is a low-molecular-weight polybutadiene with isocyanate groups placed 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. Tetramethylthiuram disulphide (TMTD, Sigma-Aldrich) was used as an accelerator and MgO (Merck) was utilized as an activator of the vulcanization reaction. Dibutyltin dilaurate (DBTL, Sigma-Aldrich) in the form of 10% paraffinic solution was used as a catalyst of the isocyanate reaction. Glycerol and sulphur (Lach-Ner, Czech Republic) were used as crosslinking agents.

Three types of glass fiber grid-lattice fabrics V240, V301, and V500 (Saint-Gobain Vertex, Czech Republic) were used as the reinforcement of composites in this study. All the utilized glass fiber fabrics were manufactured from glass fiber roving having the diameter of elementary fibers equal to 9–17 μm, made of aluminium-borate-silicate glass E-Eutal with the maximum content of alkali equal to 1%. The basic parameters of the investigated glass fiber fabrics are summarized in Table II.

Preparation and evaluation of matrixes

The matrixes comprising variable content of sulphur (0–40 phr) were prepared by crosslinking of the polybutadiene KRASOL LBD 3000 using glycerol and sulphur as follows. The solid materials (sulphur, MgO, and TMTD) were milled together using a porcelain mortar and sifted to obtain a narrow particle size distribution. All the starting materials (see Table III) were then mixed with the polybutadiene at 40°C using a hook-shaped mixer. The mixture was then poured into a hot mold 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) heated at a temperature 150°C and a pressure 2.8 MPa for 4 h. After this period, the main crosslinking reaction was completed, and the vulcanization reaction between unsaturated polybutadiene chains and sulphur took place.

The neat matrixes were evaluated from the point of view of mechanical properties (tension, flexure, Charpy impact strength, and Brinell hardness), electrical properties (volume resistance, surface resistance, permittivity, loss factor, dielectric breakdown along layers, and resistance against electric arc), and glass transition temperature (T_g). Tensile modules and tensile strength values of matrixes were determined using the MTS-4/M universal testing machine (Sintech—MTS Systems Corporation) at a crosshead speed of 5 mm/min. Tests were carried out

TABLE III
Composition of Matrixes

Sulphur content (phr)	0	5	10	15	20	25	30	35	40
Polybutadiene(g)	98.00	90.62	86.70	83.09	79.78	76.72	73.88	71.25	68.80
Glycerol (g)	2.49	2.31	2.21	2.12	2.03	1.95	1.89	1.81	1.76
Sulphur (g)	–	4.53	8.67	12.46	15.95	19.18	22.16	24.94	27.52
TMTD (g)	–	1.81	1.73	1.66	1.59	1.53	1.48	1.42	1.38
MgO (g)	–	0.91	0.87	0.83	0.80	0.77	0.74	0.71	0.69
DBTL, 0,5 % active matter in toluene, (drops)	10	10	9	8	8	7	7	6	6

TABLE IV
Content of Glass Fibre Reinforcement in Composite Test Samples

	Type of Glass Fibre Fabric					
	V240		V301		V500	
Theoretical glass content (wt %)	No. of plies	Real glass content (wt %)	No. of plies	Real glass content (wt %)	No. of plies	Real glass content (wt %)
60	15	62	11	62	7	59
70	18	70	14	70	9	70
80	21	78	17	80	11	78
90	24	85	20	89	13	88

according to ČSN EN ISO 527. The sample size used for the tensile tests was 150 × 10 × 4 mm. Flexural properties were evaluated using a three-point bending test according to ČSN EN 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. Impact strength measurements were carried out according to ČSN EN ISO 179 using the VEB 400/69/40 testing machine (Werkstoffprüfmaschinen Leipzig, Germany). The sample size used for the test was 50 × 6 × 4 mm. Hardness testing was carried out according to ČSN EN ISO 2039-1 by the VEB 300/22 tester (Werkstoffprüfmaschinen Leipzig, Germany). All the measurements of mechanical properties were carried out at ambient temperature 10 times for each type of matrix to check the reproducibility.

The testing of electrical properties of matrixes was carried out according to ČSN EN ISO 3915. The sample size used for all the electrical measurements was 75 × 50 × 4 mm. Volume and surface resistance measurements were performed at a voltage 500 V for 60 s on samples without any conditioning and on samples conditioned for 96 h at 35°C and 90% relative humidity. Permittivity and loss factor measurements were carried out at the alternating current frequency 1 MHz on samples without conditioning and on samples conditioned for 40 h at ambient temperature and 50% relative humidity. The dielectric breakdown along layers and resistance against electric arc were determined for samples immersed in water at a temperature 50°C for 48 h.

Glass transition temperatures of the matrixes were determined by means of thermomechanical analysis using the TMA CX04R instrument (R.M.I., Pardubice, Czech Republic) in the range from −60 to 150°C and the heating/cooling rate of 5°C/min. The second heating curve was used for T_g detection.

Preparation and evaluation of composites

On the basis of measurements mentioned above, all the composite materials were based on the polybutadiene matrix containing 20 phr of sulphur. The optimum matrix composition is discussed below. Composite materials comprising reinforcement made of glass fiber grid-lattice fabrics V240, V301, and V500, respectively, were prepared. The theoretical and real content of glass fiber reinforcement in the composite samples is shown in Table IV. All the starting materials (see Table III) were mixed with the polybutadiene at 40°C. The composites were fabricated by subsequent placing of individual fabric plies in the mold. The polybutadiene mixture was applied onto

TABLE V
Tensile and Flexural Properties of Matrixes Varying in the Sulphur Content

Sulphur content (phr)	Tensile modulus (MPa)	Tensile strength (MPa)	Flexural modulus (MPa)	Flexural strength ($kJ \cdot m^{-2}$)
0	1.32	1.12	13.88	0.38
5	7.58	2.28	60.22	1.96
10	37.21	6.98	98.10	2.77
15	1300.01	24.19	1378.27	36.91
20	1940.59	25.47	2117.14	63.89
25	2001.17	30.25	2486.33	75.73
30	2177.03	31.08	2789.97	66.83
35	2315.66	24.11	2935.67	78.09
40	2572.03	24.08	3157.59	84.03

TABLE VI
Impact Strength, Hardness and Glass Transition Temperatures of Matrixes Varying in the Sulphur Content

Sulphur content (phr)	Impact strength ($kJ \cdot m^{-2}$)	Hardness 10 (s)	Hardness 60 (s)	T_g (°C)
0	Not measurable	24.52	24.25	−30.5
5	Not measurable	30.57	23.29	6.0
10	33.65	31.04	23.58	23.0
15	14.95	191.17	150.41	39.5
20	8.51	272.24	211.58	61.3
25	6.55	325.64	285.22	91.8
30	3.90	332.46	297.87	97.1
35	3.59	356.04	317.42	110.4
40	3.29	362.60	327.45	118.0

TABLE VII
Survey of Electric Properties of Vulcanized Matrixes

Property	Conditioning	Sulphur Content (phr) 0	10	20	30	40
Volume resistance (MΩ·cm)	No	2×10^{10}	4.2×10^{9}	2.6×10^{9}	2.4×10^{9}	6.9×10^{9}
	Yes	4.4×10^{9}	4.6×10^{8}	2.3×10^{9}	1.3×10^{9}	3.4×10^{9}
Surface resistance (MΩ)	No	1.9×10^{11}	1.9×10^{10}	5.1×10^{9}	2.2×10^{10}	1.5×10^{10}
	Yes	6.1×10^{9}	1.2×10^{9}	1.3×10^{8}	9.4×10^{9}	1.1×10^{10}
Permittivity	No	2.76	2.76	2.92	2.8	2.63
	Yes	2.78	2.88	2.92	2.8	2.38
Loss factor	No	0.024	0.018	0.0077	0.0071	0.0057
	Yes	0.024	0.018	0.0071	0.0074	0.0074
Dielectric breakdown along layers (kV)	Yes	>40	>40	>40	>40	>40
Resistance against electric arc (s)	Yes	>60	>60	>60	>60	>60

glass fabric surface by the calender Collin W 110 (Collin, Germany). The mold was heated at 90°C for 45 min and then put into the vulcanizing press P 11-E at a pressure 2.8 MPa and allowed to cure at a temperature 150°C for 4 h. Mechanical properties (tension, flexure, Charpy impact strength and Brinell hardness) of the composites reinforced with fabrics V240, V301, and V500, respectively, were evaluated and compared with those of the neat matrix.

RESULTS AND DISCUSSION

Properties of matrixes

Optimum sulphur content needed for vulcanization of polybutadiene matrix was investigated to achieve the final matrix composition with enhanced mechanical properties and without loosing perfect electroinsulating properties. The compromise between improvement of tensile and flexural properties and a drop in the impact strength was the crucial criterion.

Tables V and VI summarize mechanical properties of matrixes varying in the content of sulphur. It is evident that matrixes containing higher amount of sulphur exhibited higher values of flexural modulus and flexural strength, tensile modulus and tensile strength, and higher values of hardness as well, but their impact strength was lowered. Samples containing sulphur at the concentration 0 and 5 phr were so soft and tough that their impact strength could not be measured. It can be summarized that samples comprising low amounts of sulphur are soft and tough, which corresponds to low T_g values (see Table VI). The higher the sulphur content, the denser crosslinked network was formed, which is manifested by brittle and hard materials having a high value of T_g. Electric properties of the vulcanized matrixes are listed in Table VII. Values of volume resistance, surface resistance, permittivity, loss factor, dielectric breakdown along layers, and resistance against electric arc given for the individual matrixes indicate that all the investigated materials were excellent insulators. Only a negligible decrease in electric-insulating properties at higher sulphur concentration was found. The matrix composition with the optimum sulphur content 20 phr was chosen for

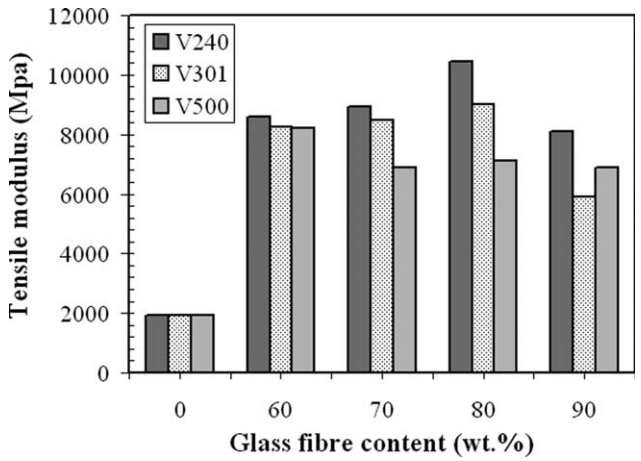

Figure 1 Dependence of the content of glass fibers on the tensile modulus of composite materials varying in the type of glass fiber fabric reinforcement.

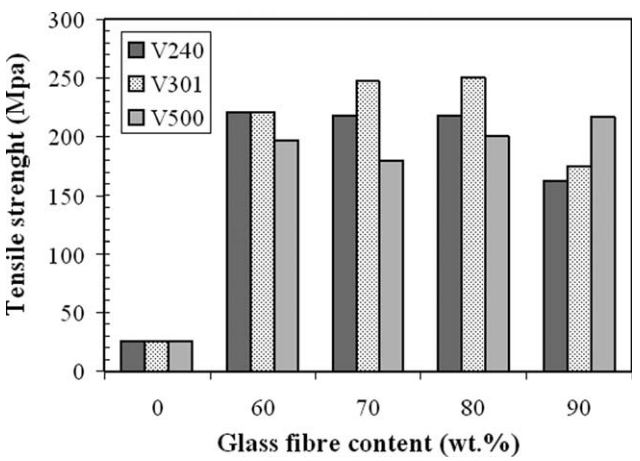

Figure 2 Dependence of the content of glass fibers on the tensile strength of composite materials varying in the type of glass fiber fabric reinforcement.

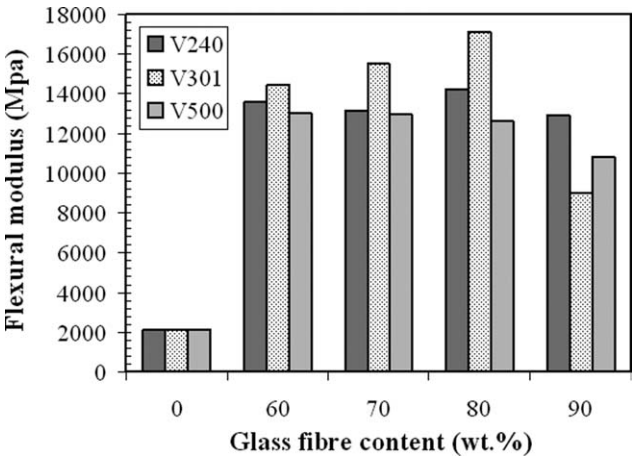

Figure 3 Dependence of the content of glass fibers on the flexural modulus of composite materials varying in the type of glass fiber fabric reinforcement.

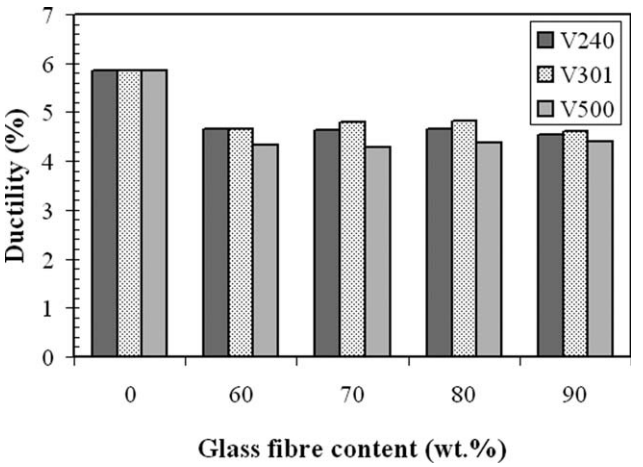

Figure 5 Dependence of the content of glass fibers on the ductility of composite materials varying in the type of glass fiber fabric reinforcement.

the subsequent research. The matrix vulcanized by 20 phr of sulphur was chosen from the point of view of such mechanical properties of composites that enable to compare effects of different matrices in composites as well as easy processing of uncured matrix.

Properties of composites

Figures 1–9 illustrate results of mechanical property measurements for composite materials varying in the type and content of glass fiber reinforcement. The results indicate that both the tensile and flexural properties and the impact strength of composites were improved significantly by glass fiber reinforcement in contrast to the neat matrix (see Figs. 1–7). It was shown that the ductility of fiber-reinforced composites was not affected by the glass fiber content. Figure 6 demonstrates a drop of load deflection of composites with the increasing glass fiber content. Only a slight increase in hardness of reinforced vulcanizates was observed when comparing the values of reinforced and neat matrix (see Figs. 8 and 9). It was shown as well that all the tested mechanical properties of composites improved until the content of glass fibers reached 80 wt %, whereupon a drop in tested properties occurred at the glass content 90 wt %. This phenomenon was apparently caused by the effect of an insufficient amount of polybutadiene, which did not allow the formation of a coherent polymeric layer between individual fiber plies and resulted in a poor cohesion of the composite material.

On the basis of all the results obtained for vulcanizates varying in the glass fiber content, it can be stated that the optimum content of glass fiber

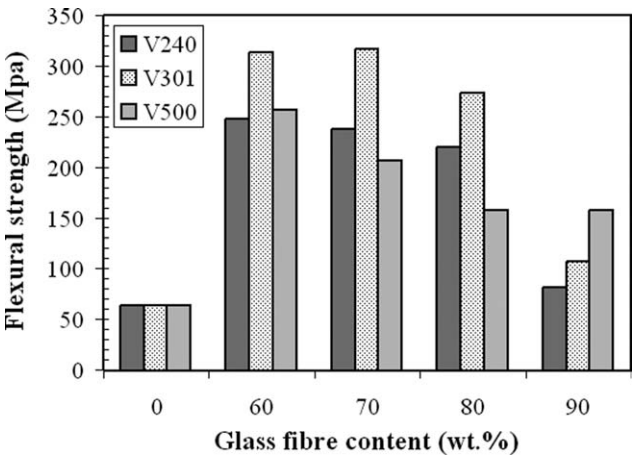

Figure 4 Dependence of the content of glass fibers on the flexural strength of composite materials varying in the type of glass fiber fabric reinforcement.

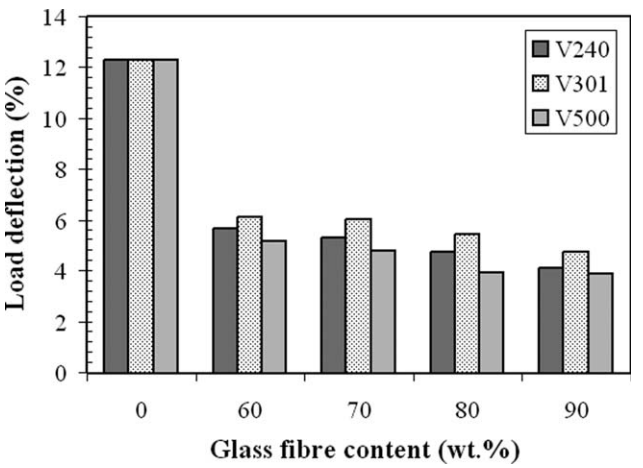

Figure 6 Dependence of the content of glass fibers on the load deflection of composite materials varying in the type of glass fiber fabric reinforcement.

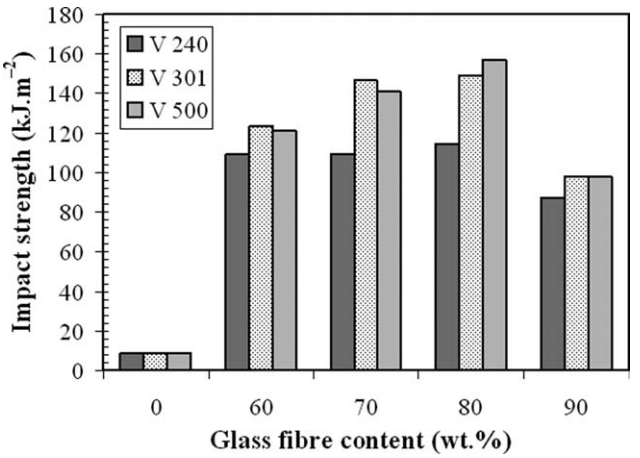

Figure 7 Dependence of the content of glass fibers on the impact strength of composite materials varying in the type of glass fiber fabric reinforcement.

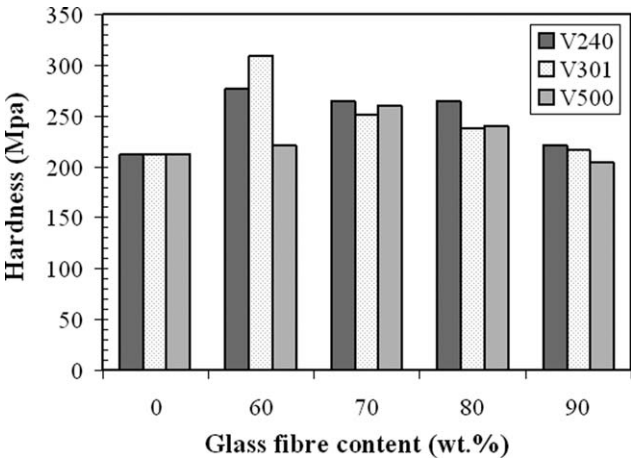

Figure 9 Dependence of the content of glass fibers on the hardness values (straining time 60 s) of composite materials varying in the type of glass fiber reinforcement.

reinforcement is in the range of 70–80 wt %. Further, when comparing the results for three different types of reinforcing glass fiber fabrics, namely V240, V301, and V500, the fabric V301 was found to be the most suitable type as the reinforcement of polybutadiene-based vulcanizates.

As no data concerning vulcanized liquid polybutadiene-based composites were found in literature, the mechanical properties of the tested polybutadiene composites were compared with mechanical characteristics of composites based on unsaturated polyesters, vinylester resins, and low-molecular-weight epoxides cured with polyamines.[15–17] This comparison has shown that the vulcanized liquid polybutadiene-based composites exibited similar properties as above-mentioned ones. These promising results indicate that optimizing the sulphur content and matrix-reinforcement ratio should lead to very good properties of vulcanized liquid polybutadiene-based composites. This will be investigated in the next period.

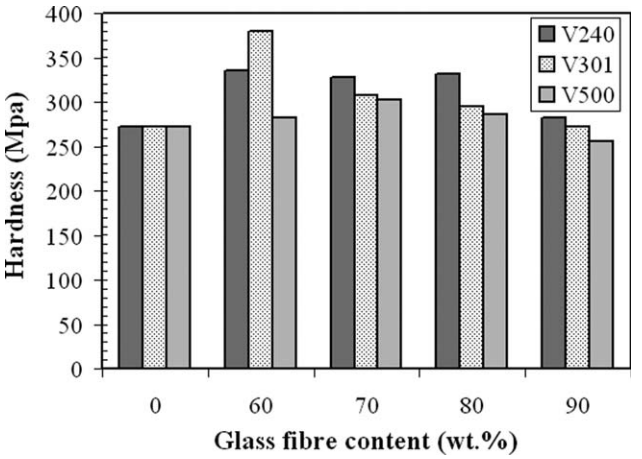

Figure 8 Dependence of the content of glass fibers on the hardness values (straining time 10 s) of composite materials varying in the type of glass fiber fabric reinforcement.

CONCLUSIONS

Polybutadiene bearing isocyanate endgroups was investigated as a matrix for glass fiber-reinforced composite materials with enhanced mechanical properties and without loosing perfect electroinsulating properties. It was found that the sulphur-vulcanized polybutadiene exhibited improved mechanical properties and retained an excellent electroinsulating character. The matrix with the sulphur content 20 phr was chosen as the optimum composition. It was shown that both the tensile and flexural properties and the impact strength of composites were improved significantly by glass fiber reinforcement in contrast to the neat polybutadiene matrix. The optimum content of glass fiber reinforcement was in the range of 70–80 wt %. Among all the tested fabrics, the fabric V301 characterized by the medium values of fabric weight and fabric ply thickness was found to be the most suitable type as the reinforcement for polybutadiene-based vulcanizates.

References

1. Dreyfuss, P. In Polymeric Materials Encyclopedia; Salomone, J. C., Ed.; CRC Press: Boca Rato, FL, 1996; Vol. 8, pp 5657–5663.
2. Kokta, B.V.; Michalkova, D.; Fortelny, I.; Krulis, Z. Polym. Adv. Technol 2007, 18, 106.
3. Suresha, B.; Chandramohan, G.; Mohanram, P. V. Polym. Compos 2009, 30, 1106.
4. Cirino, M.; Friedrich, K.; Pipes, R. B. Wear 1988, 121, 127.
5. Bijwe, J.; Logan, C. M.; Tewari, U. S. Wear 1999, 145, 77.
6. Mathew, G.; Thomas, S.; Kuriakose, B. J. Elast. Plast 1997, 29, 163.

7. Kaynak, C.; Arikan, A.; Tincer, T. Polymer 2003, 44, 2433.
8. Suwanprateeb, J. Polym. Plast. Technol. Eng 2000, 39, 83.
9. Demirhan, E.; Dincer, S.; Sarac, H. I. Polym. Plast. Technol. Eng 1994, 33, 83.
10. Fu, T.; Yu, L.; Wang, Z.; Yu, W.; Zhao, Ch.; Zhong, S.; Cui, J.; Shao, K.; Na, H. Polym. Compos 2009, 30, 948.
11. Sever, K.; Sarikanat, M.; Seki, Y.; Tavman, I. H. Polym. Compos 2009, 30, 1251.
12. Kim, J.; Shioya, M.; Kobayashi, H.; Kaneko, J.; Kido, M. Compos. Sci. Technol 2004, 64, 2221.
13. Unal, H.; Mimaroglu, A. J. Reinforc. Plast. Compos 2004, 23, 461.
14. Synthos Kralupy. Product data sheet of Krasol LBD 3000, 1995.
15. Ehrenstein, G. W. Polymeric Composite Materials; Scientia: Prague, 2009; pp 326–327.
16. Reinhart, T. J. Engineered Materials Handbook Vol. 1: Composite; ASM International: Ohio, 1987, p 92.
17. Lidařík, M. Epoxide Resins; SNTL: Prague, 1983; pp 551, 556.