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THE INFLUENCE OF POLYESTER RESIN COMPOSITION ON FIBER-MATRIX INTERPHASE PROPERTIES

VPLIV SESTAVE NENASIČENE POLIESTRSKE SMOLE NA INTERAKCIJE S STEKLENIMI VLAKNI

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Properties of glass-fiber reinforced polyesters depend on resin and glass type, on fiber weight fraction, on processing, and on structural variables. The tensile properties of different types of E-glass-fiber chopped strand mat reinforced polyester laminates were analysed. The influence of unsaturated polyester resins composition, styrene content and type of glass-fiber on interphase properties, which dictate polyester laminate tensile strength, were determined and correlated.

Key words: unsaturated polyester resin, polyester laminates, interphase properties, tensile strength

Uporabne lastnosti poliestrskih kompozitov so odvisne od vrste in sestave nenasičene poliestrske smole, od vrste in vsebnosti steklenih vlaken v kompozitu in načina njihove izdelave. Različnim tipom laminatov iz nenasičene poliestrske smole in polsti iz steklenih vlaken smo določili natezne lastnosti. Vpliv sestave nenasičene poliestrske smole, vsebnosti stirena v njej in vrste steklenih vlaken na interakcije med nenasičeno poliestrsko smolo in steklenimi vlakni smo določili z meritvami in primerjavo nateznih trdnosti poliestrskih laminatov.

Ključne besede: nenasičena poliestrska smola, poliestrski laminati, interakcije s steklenimi vlakni, natezna trdnost

1 INTRODUCTION

Fibrous composite materials are viewed as having three components: fiber, matrix and interface (interphase)[1]. Composites mechanical properties are controlled by the strength and the elastic properties of the fibers, the matrix and the fiber-matrix bond which governs the stress transfer[2,3]. Any of these elements can be a 'weak link' that could strongly affect the mechanical properties of the material. If there is weaker adhesion at the interface, the stress transfer between fibre and matrix is reduced[2].

The nature and properties of the interface are unique to each fiber-matrix system. Adhesion between fiber and matrix can be attributed to some combination of the following phenomena:

- Adsorption and wetting
- Mechanical adhesion
- Interdiffusion
- Electrostatic attraction
- Chemical bonding

The strength of the final bond will reflect any chemical reaction that has occured between fiber, fiber coating and resin during processing. Glass-fibers first react with silane or other coupling agent which later couples to the matrix resin via one or more reactive groups[4,5] (**Figure 1**).

Unsaturated polyester resins (UPR) are solutions of unsaturated polyesters in copolymerizing solvents such as styrene. Literature sources propose glass-fiber's silane coupling agent's reaction with styrene or with unsaturated polyester and further participation in forming three-dimensional network of cured polyester[6,7].

The strength, stiffness and toughness of the interfacial bond all affect the composite's ultimate properties and the mechanisms by which it fails. The fracture energy derived from tensile strength test, is considered as a primary measure of interfacial bond strength[1,4].

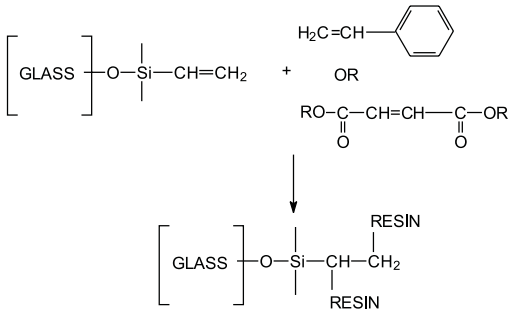

Figure 1: Chemical reaction between glass-fiber vinylsilane coupling agent with styrene or with unsaturated polyester
Slika 1: Kemijska reakcija vinilsilanskega sklopitvenega reagenta steklenih vlaken s stirenom ali z nenasičenim poliestrom

The aim of this paper was to point out the influence of unsaturated polyester composition and styrene content on UPR-E-glass-fiber interfacial properties; furthermore, to determine UPR composition with the most significant effect on interfacial properties.

2 EXPERIMENTAL

2.1 Experimental design for synthesis of UPR

The experiment was designed using Half-fraction Factorial Central Composite Design[8,9].

The compositions **(Table 1)** of UPR were varied using three factors (A, B and C) which were set at two levels: low (-) and high (+). Centre (reference) composition of the resin (0, 0, 0), a commonly used composition of UPR for hand lay-up applications, was also synthesised **(Table 2)**.

Table 1: Experimental design
Tabela 1: Eksperimentalni načrt

VARIABLE	COMPONENTS	LEVEL	RATIO
A	PHA : MA	- 0 +	1 : 0.5 1 : 1 1 : 1.5
B	PG : DEG	- 0 +	1 : 0.5 1 : 1 1 : 1.5
C	w (styrene)	- 0 +	35% 40% 45%

Table 2: Synthesised UPR composition
Tabela 2: Sestava sintetiziranih nenasičenih poliestrskih smol

SYNTHESIS	VARIABLES		
	A	B	C
1	0	0	0
2	+	-	-
3	-	-	+
4	-	+	-
5	+	+	+

2.2 Reactants

The compositions of UPR were based on phthalic anhydride (PHA), maleic anhydride (MA), propylene glycol (PG), diethylene glycol (DEG) and styrene.

2.3 Synthesis of UPR

The UPR were synthesised by the azeotropic process. The ratio between acid anhydrides and glycols was 1:1.1. As azeotropic agent toluene in 5wt% amount of the total weight of reactants was used. The reactions proceeded at 200°C until the acid number dropped to about 43 mg KOH / g(resin). The acid number was determined by titrating the solutions of unsaturated polyester in toluene:ethanol = 2:1, with 0.1N KOH in toluene:ethanol = 2:1 solution using phenolphtalein indicator. At the end of the reaction the resulting unsaturated polyester was stabilised by hydroquinone in 0.02wt% of the total weight of reactants and after cooling to 90°C intermixed with styrene[10,11].

2.4 Forming of polyester laminates and tensile testing

Polyester laminates (L **O** and L **V**) were formed from two types of E-glass-fiber chopped strand mat (CSM) which differ in amount of glass-fiber coupling agent. Its amount on CSM **O** is 3.61 ± 0.01 wt% and on CSM **V** 4.45 ± 0.02 wt%.

The polyester laminates were formed via mold hand lay-up technique. Four layers of CSM with weight 300 g/m^2 were wetted with UPR. Styrene solution of Co octoate and methyl ethyl ketone peroxide were applied as UPR initiator system. All laminates were released after 4 hours and were allowed to cure for 24 hours at room temperature before being given a post cure treatment at 80°C for 16 hours.

The laminates were afterwards cut and their tensile properties were tested in accordance with standard ISO 527. Tensile properties were characterised by using Karl Frank tensile testing machine at a test speed 2 mm/min. The deformation was measured at the central part of the sample using inductive measurer of deformation (HBM - D4).

The glass-fiber content of the samples was determined by resin burnoff at 530°C for 8 hours.

In a small scale linear influence of glass-fibre content on tensile properties of polyester laminates was expected, therefore all mesaured tensile properties were adapted to the 35 wt% glass-fiber content in laminates, which represents the average content of glass-fiber in tested samples.

The unsaturated polyester resins were cured and their tensile properties were measured following the same method.

2.5 Evaluation of effects on interphase properties

The effects of UPR composition on interaction with E-glass-fiber were evaluated by comparing polyester laminate tensile responses with UPR tensile responses.

It can be formulated as follows:

$$\textit{Laminate response / Resin response} = \text{L}\mathbf{O}\text{R} / \text{RR} \text{ or } \text{L}\mathbf{V}\text{R} / \text{RR} \quad (1)$$

Laminate response - L**O**R (CSM **O**) or L**V**R (CSM **V**): average value for tensile property of laminates formed from UPR with the same level of selected variable

Resin response - RR: average value for tensile property of UPR with the same level of selected variable

Table 3: Tensile properties of UPR and of two types of polyester laminates
Tabela 3: Natezne lastnosti zamrežene nenasičene poliestrske smole in dveh vrst poliestrskih laminatov

MATERIAL	TENSILE PROPERTIES	SYNTHESIS				
		1	**2**	**3**	**4**	**5**
UPR	Tensile E-modulus/MPa	3362±191	3374±36	3432±95	1797±100	3230±183
	Tensile strength/MPa	53±3	71±2	58±4	35±0,5	60±10
	Elongation at break/%	1.9±0.2	3.2±0.4	2.4±0.25	4.5±0.1	2.6±0.8
L O	Tensile E-modulus/MPa	8440±352	7647±510	7985±500	6071±486	8220±499
	Tensile strength/MPa	110±3	108±8	112±6	110±10	111±8
	Elongation at break/%	1.8±0.1	1.8±0.2	1.8±0.2	2.0±0.3	1.8±0.2
L V	Tensile E-modulus/MPa	8982±176	9167±425	8247±228	6403±538	8120±607
	Tensile strength/MPa	98±5	86±4	96±5	104±5	98±5
	Elongation at break/%	1.5±0.1	1.4±0.1	1.5±0.1	2.1±0.1	1.5±0.05

Table 4: The influence of PHA:MA ratio: (a) tensile strenghts, (b) tensile E-modulus
Tabela 4: Vpliv razmerja med ftalanhidridom in malein anhidridom; povprečne vrednosti: (a) natezne trdnosti, (b) natezni E-moduli
(a)

SYNTHESIS	LEVEL	RR/MPa	LOR/MPa	LOR / RR	LVR/MPa	LVR / RR
3.4	-	46.5	111	2.4	100	2.2
1	0	53	110	2.1	98	1.8
2.5	+	65.5	109.5	1.7	92	1.4

(b)

SYNTHESIS	LEVEL	RR/MPa	LOR/MPa	LOR / RR	LVR/MPa	LVR / RR
3.4	-	2614.5	7028	2.7	7325	2.8
1	0	3362	8440	2.5	8982	2.7
2.5	+	3302	7933.5	2.4	8643.5	2.6

Table 5: The influence of PG:DEG ratio: (a) tensile strenghts, (b) tensile E-modulus
Tabela 5: Vpliv razmerja med propilenglikolom in dietilenglikolom; povprečne vrednosti: (a) natezne trdnosti, (b) natezni E-moduli
(a)

SYNTHESIS	LEVEL	RR/MPa	LOR/MPa	LOR / RR	LVR/MPa	LVR / RR
2.3	-	64.5	110	1.7	91	1.4
1	0	53	110	2.1	98	1.8
4.5	+	47.5	110.5	2.3	101	2.1

(b)

SYNTHESIS	LEVEL	RR/MPa	LOR/MPa	LOR / RR	LVR/MPa	LVR / RR
2.3	-	3403	7816	2.3	8707	2.6
1	0	3362	8440	2.5	8982	2.7
4.5	+	2513.5	7028	2.8	7261.5	2.9

Table 6: The influence of styrene content: (a) tensile strenghts, (b) tensile E-modulus
Tabela 6: Vpliv vsebnosti stirena; povprečne vrednosti: (a) natezne trdnosti, (b) natezni E-moduli
(a)

SYNTHESIS	LEVEL	RR/MPa	LOR/MPa	LOR / RR	LVR/MPa	LVR / RR
2.4	-	53	109	2.0	98	1.8
1	0	53	110	2.1	98	1.8
3.5	+	59	111.5	1.9	97	1.6

(b)

SYNTHESIS	LEVEL	RR/MPa	LOR/MPa	LOR / RR	LVR/MPa	LVR / RR
2.4	-	2585.5	6859	2.6	7785	3.0
1	0	3363	8440	2.5	8982	2.7
3.5	+	3331	8102.5	2.4	8183.5	2.4

3 RESULTS AND DISCUSSION

The influence of UPR composition on UPR-E-glass-fiber interfacial properties was characterised by tensile strength measurements of polyester laminates (**Table 3**).

In **Figure 2a** are presented UPR tensile strength responses (RR) and polyester laminate tensile strength responses (LOR and LVR) as a function of PHA:MA ratio, in Figure 2b, as a function of PG:DEG ratio as well as a function of styrene amount in **Figure 2c**.

As the amount of MA is higher and as the level of unsaturation in unsaturated polyester is increased, UPR tensile strength increases, and laminates tensile strength decreases (**Figure 2a, Table 4a**).

Figure 2b, Table 5a show decrease in tensile strength and **Table 5b** increased flexibility of the UPR at increasing amount of incorporated DEG. The UPR flexibility is increased due to ether glycols lack of steric protection given to ester linkages. The laminate tensile strength subsequently increases high level of DEG amount (level +) being in consideration.

The influence of styrene content on tensile strengths of polyester laminates in limits within 35% and 45% amount, is less significant. (**Figure 2c and Table 6a**).

Results in **Table 4b**, **Table 5b** and **Table 6b** show that the E-modulus of laminates follow the E-modulus of the resin. The LOR / RR and the LVR / RR values for E-modulus are higher than for tensile strength. Reinforcing UPR with glass-fiber has larger effect on E-modulus of laminates than on their tensile strengths. This is a consequence of the reduced glass-fiber tensile strength when incorporated in resin.

Interfacial properties, as a function of UPR composition, were characterised by results of polyester laminate tensile strengths, as a measure of interfacial bond strengths. The mat reinforced material is treated as isotropic[12]. Tensile elongation of laminates is dominated by reinforcement and the contribution of the cured resin is masked, while strenghts are largely determined by the resin[13].

From **Figure 2a,b,c** it is evident that composition of UPR affects the tensile strength of polyester laminate in accordance with changing resin components' ratio influence on resin flexibility. The difference between two types of CSM is noticeable, the influences of UPR composition are larger for polyester laminates reinforced with CSM **V** with higher amount of glass-fiber coupling agent, though the values of tensile strengths are lower than for CSM **O** reinforced polyester laminates.

From the correlations of different compositions of UPR follows that increased flexibility of UPR improves interfacial properties of corresponding polyester laminates.

Since deducing adhesive strengths from tensile strength measurements is a demanding task, results can only be evaluated by means of comparision.

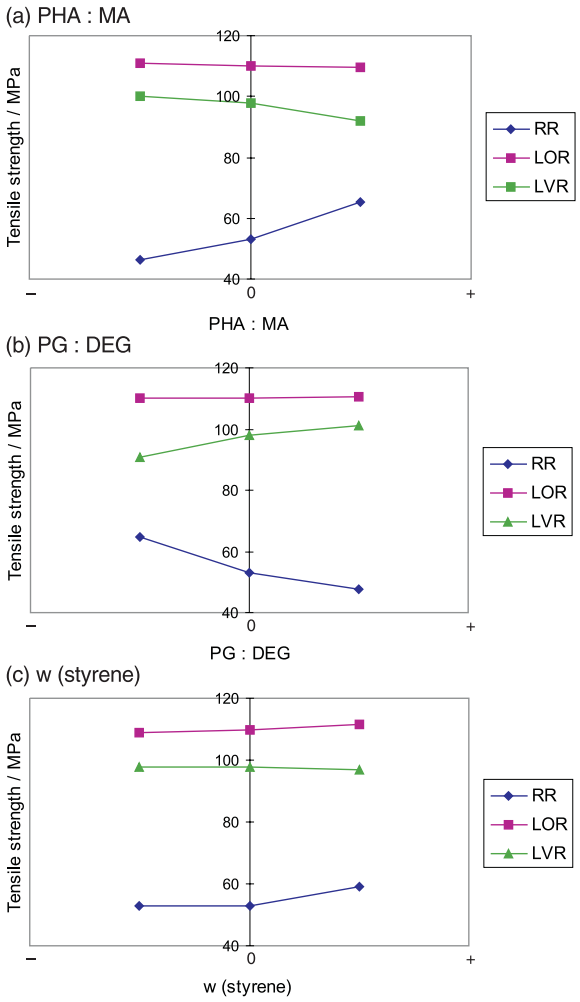

Figure 2: Tensile strength responses of UPR and of polyester laminates as a function of UPR composition

Slika 2: Povprečne vrednosti nateznih trdnosti nenasičene poliestrske smole in poliestrskih laminatov v odvisnosti od sestave nenasičene poliestrske smole

4 CONCLUSIONS

The influence of UPR composition on UPR - E-glass-fiber interfacial properties was characterised by polyester laminates tensile strength.

Tensile strength measurements results and their correlation showed that the largest effect on increasing tensile strength of polyester laminates have resins with low amount of MA, high amount of DEG and low amount of styrene. Polyester laminates tensile strength, as a measure of interfacial bond strength, is therefore significantly enlarged in the case of flexible resins used for laminate forming.

The improving effect of flexible resins on interaction with glass-fiber coupling agent is probably due to reduced stereohindrance for their interaction.

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