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KOMPOZYTY
COMPOSITES

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EPOXY-VINYL ESTER MATERIALS

The work is the continuation of an investigation conducted in the Polymer Institute concerning the modification of epoxy resins with the aim of utilizing these materials for production by means of Resin Transfer Moulding (RTM). In the work, the mechanical strengths and glass transition temperature were reported for epoxy-vinylester compositions/composites. The following kinds of epoxy resin were used: Epidian 6 or Ampreg 22 hardened with 1-ethylimidazole and vinylester resins; VE-2MM or Atlac 580 ACT cured with t-butyl perhydroxide.

In an earlier paper, we proved that modified epoxy resin with vinylester resin causes a decrease in viscosity and makes it possible to form an Interpenetrating Polymer Network (IPN). This described modification leads to an improvement of mechanical durability, especially with a content of vinylester resin in the range of 30÷50 wt.%. The selected curing agents made it possible to obtain a Simultaneous Interpenetrating Network for the components.

Keywords: **epoxy-vinylester composition/composites, epoxy resin, vinylester resin, Resin Transfer Moulding, Interpenetrating Polymer Network**

MATERIAŁY EPOKSYDOWO-WINYLOESTROWE

Prezentowana praca jest kontynuacją badań prowadzonych w Instytucie Polimerów związanych z modyfikacją żywic epoksydowych w celu obniżenia lepkości i możliwości ich wykorzystania w formowaniu wyrobów z użyciem metody RTM. Opisano wpływ wprowadzenia żywicy winyloestrowej na wytrzymałość mechaniczną i temperaturę zeszklenia kompozytów epoksydowo-winyloestrowych. W badaniach zostały wykorzystane żywice epoksydowe: Epidian 6 i Ampreg 22 utwardzane 1-etyloimidazolem oraz winyloestrowej: VE-2MM i Atlac 580 ACT sieciowane wodoronadtlenkiem t-butylu.

We wcześniejszych pracach zespołu wykorzystano do modyfikacji żywicy epoksydowej żywicę winyloestrową w celu obniżenia lepkości układu oraz umożliwienia tworzenia się wzajemnie przenikających się sieci polimerowych typu IPN, przy czym użyto innego układu środków sieciujących.

Opisywana modyfikacja prowadzi do poprawy wytrzymałości mechanicznej, szczególnie w przypadku zawartości żywicy winyloestrowej od 30 do 50% wag. Odpowiedni dobór środków sieciujących umożliwia utworzenie się jednocześnie przenikających się sieci polimerowych i jednoczesną poprawę wytrzymałości mechanicznej.

Słowa kluczowe: **kompozycje/kompozyty epoksydowo-winyloestrowe, żywica epoksydowa, żywica winyloestrowa, formowanie techniką RTM, wzajemnie przenikające się sieci polimerowe**

INTRODUCTION

This work describes epoxy-vinylester compositions with imidazole as a curing agent. The modifications of epoxy resin with vinylester resin ought to improve mechanical and thermal strengths and reduce the viscosity of the compositions [1-6]. The use of two independent polymer networks and two different curing systems allowed the formation of an Interpenetrating Polymer Network type SPN. Generally, from thermosetting resin, two kinds of IPN can be formed: Sequential (IPN) or Simultaneous (SIN). In the first case, polymer network I is synthesized, then monomer II with a crosslinker and activator are swollen into network I and polymerized *in situ*. In the second case, the monomers and/or prepolymers plus crosslinkers and activators of both components are mixed, followed by simultaneous polymerization *via* non-interfering reactions [1-4]. Typical syntheses involve chain and step polymerization kinetics. While both polymerizations proceed simultaneously, the rates of the reactions are rarely identical [2].

In this work, the synthesis of epoxy-vinylester composites and the mechanical properties of these materials are described.

MATERIALS AND METHODS

The epoxy resins used were Epidian 6 - E6 (a product of the Chemical Works “Organika Sarzyna” in Nowa Sarzyna) and Ampreg 22 - AM22 (a product of the

SP “Gurit” System). The vinylester resins that were used were VE-2MM - 2MM (a product of the Chemical Works “Organika Sarzyna” in Nowa Sarzyna) and Atlac 580 ACT - AT a product of “DSM Composite” Resins AG. The curing systems were mixtures of 1-ethylimidazole and t-butyl perhydroxide in the amount of 1 phr of resin. The epoxy compositions were hardened at 120°C for 2 hours.

The tensile and bending strengths were measured in accordance with PN-EN ISO527-1 (speed rate of 5 mm/min) and PN-EN ISO178 (speed rate of 1 mm/min) standards by means of an Instron 4026 testing machine from the Instron Corporation.

The glass transition temperatures were estimated using a dynamic mechanical thermal analyzer DMTA Mark II, Polymer Laboratories (frequency 1 Hz, speed rate of 3°C/min).

RESULTS

Mechanical properties - Tensile strength

In the following tables and figures, the results of the tensile strengths for epoxy-vinylester composites are shown.

The tensile strengths were in the range of 24.6 MPa for epoxy resin Epidian 6 and 27.4 MPa for vinylester resin VE-2MM to 44.0 MPa for epoxy-vinylester materials with 50 wt.%. content of vinylester resin (Tab. 1). The tensile strengths of the epoxy-vinylester composites were from 26 to 78%, higher than this parameter for the epoxy material. The standard deviations are in the range of 3.0 to 10.2 MPa. Young’s Modulus of the composites ranged between 1360 and 1570 MPa.

TABLE 1. **Tensile strengths for E6/2MM epoxy-vinylester composites**

TABELA 1. **Wytrzymałość na rozciąganie kompozytów epoksydowo-winyloestrowych E6/2MM**

No.	Content of vinylester resin %	Tensile strength MPa	Std. MPa	Young’s Modulus MPa	Std. MPa
1	0	24.6	5.1	1485	140
2	30	36.4	3.0	1362	48
3	40	43.6	5.3	1570	199
4	50	44.0	6.9	1484	79
5	60	31.1	5.0	1566	230
6	70	34.4	10.2	1488	59
7	100	27.4	6.6	1445	163

The tensile strength of the materials obtained from vinylester resin Atlac 580 ACT, especially from 70 and 60 wt.% contents of this resin, were considerably lower than the composites obtained from solid resin. The highest values of these parameters were observed in composites with 40 and 30 wt.% contents of Atlac 580 ACT vinylester resin. The standard deviations are in the range of 0.6 to 13.2 MPa (Tab. 2).

TABLE 2. **Tensile strengths for AM22/AT epoxy-vinylester composites**

TABELA 2. **Wytrzymałość na rozciąganie kompozytów epoksydowo-winyloestrowych AM22/AT**

No.	Content of vinylester resin %	Tensile strength MPa	Std. MPa	Young’s Modulus MPa	Std. MPa
1	0	33.3	4.9	1445	118
2	30	49.3	6.5	1369	183
3	40	52.6	3.9	1222	84
4	50	29.5	13.2	1400	136
5	60	16.7	6.9	1143	43
6	70	4.8	0.6	1317	201
7	100	18.6	7.8	1598	63

Young’s Modulus ranged from 1150 to 1600 MPa and was generally lower than in the case of composites obtained from a solid epoxy and vinylester resin. Generally the tensile strengths of the composites obtained from the compositions with Ampreg 22 and Atlac 580 ACT were characterized by lower values than for the compositions of Epidian 6 and VE-2MM respectively.

The comparison of the tensile strengths for mixing compositions/composites and solid materials obtained from epoxy resin leads to the conclusion that it is possible to create an Interpenetrating Polymer Network.

The tensile strengths of the hardened compositions are generally higher than the composites obtained from only epoxy or vinylester resin (Figs. 1 and 2).

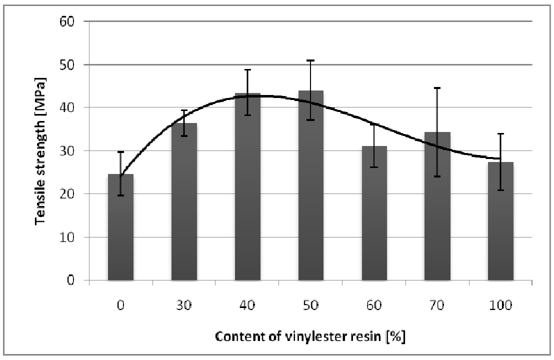

Fig. 1. Tensile strengths for E6/2MM epoxy-vinylester composites

Rys. 1. Wytrzymałość na rozciąganie kompozytów epoksydowo-winyloestrowych E6/2MM

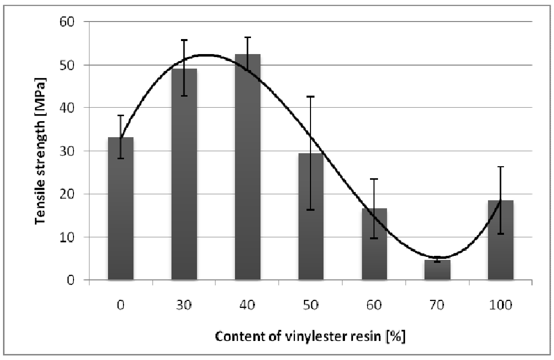

Fig. 2. Tensile strengths for AM22/AT epoxy-vinylester composites

Rys. 2. Wytrzymałość na rozciąganie kompozytów epoksydowo-winyloestrowych AM22/AT

When a definite optimum of vinylester resin content exists, maximum tensile strength is observed. In the case of the compositions with Epidian 6 and VE-2MM (Fig. 1), higher mechanical strength was obtained in a wider range of vinylester resin content (from 30 to 70 wt.%). For composites obtained from Ampreg 22 and Atlac 580 ACT (Fig. 2), higher or comparable values of this parameter were obtained for the composites with 30 to 50 wt.%. content of vinylester resin.

Mechanical properties - Bending strength

In the following tables and figures, the results of the bending strengths for epoxy-vinylester composites are presented.

The bending strengths ranged from 78.40 MPa for epoxy resin Epidian 6 and 50.46 MPa for vinylester resin VE-2MM to 138.10 MPa for epoxy-vinylester materials with 50 wt.% content of vinylester resin.

The tensile strengths for the composites of epoxy-vinylester materials ranged from 16 to 75%, and were higher than this parameter for the composites obtained from epoxy material. The standard deviation is in the range of 3.9 to 9.5 MPa (Tab. 3). The modulus of elasticity for the composites used, ranged between 2106 and 2670 MPa.

TABLE 3. **Bending strengths for E6/2MM epoxy-vinylester composites**

TABELA 3. **Wytrzymałość na zginanie kompozytów epoksydowo-winyloestrowych E6/2MM**

No.	Content of vinylester resin %	Bending strength MPa	Std. MPa	Modulus of elasticity MPa	Std. MPa
1	0	78.4	5.8	2460	44
2	30	92.7	5.5	2106	35
3	40	133.6	6.5	2598	31
4	50	138.1	3.9	2439	66
5	60	109.3	9.5	2670	68
6	70	91.5	5.0	2565	42
7	100	50.5	5.4	2539	67

The bending strengths obtained for the materials of Atlac 580 ACT vinylester resin, especially with 70% and 60 wt.%. contents of this resin, were significantly lower than for the composites obtained from solid resin. The highest values of this parameter were found for the composites with 40 and 30 wt.% contents of Atlac 580 ACT vinylester resin. The standard deviations are in the range of 1.1 to 9.5 MPa (Tab. 4).

The modulus of elasticity ranged from 1350 to 2883 MPa and was generally lower than for the composites obtained from solid epoxy and vinylester resin. Generally, the bending strengths of the composites obtained from Ampreg 22 and Atlac 580 ACT were characterized by lower values than for the compositions obtained from Epidian 6 and VE-2MM respectively.

TABLE 4. **Bending strengths for AM22/AT epoxy-vinylester composites**

TABELA 4. **Wytrzymałość na zginanie kompozytów epoksydowo-winyloestrowych AM22/AT**

No.	Content of vinylester resin %	Bending strength MPa	Std. MPa	Modulus of elasticity MPa	Std. MPa
1	0	88.8	5.9	2442	59
2	30	107.3	6.2	2103	53
3	40	116.5	3.4	2166	53
4	50	99.8	2.8	1938	54
5	60	60.3	9.5	1350	92
6	70	20.3	1.1	1956	51
7	100	62.3	5.3	2883	92

The comparison of bending strengths for epoxy-vinylester compositions/composites and compositions obtained from pure epoxy or vinylester resin (higher values for mixed compositions than epoxy or vinylester resin) leads to a statement about the possibility of creating an Interpenetrating Polymer Network.

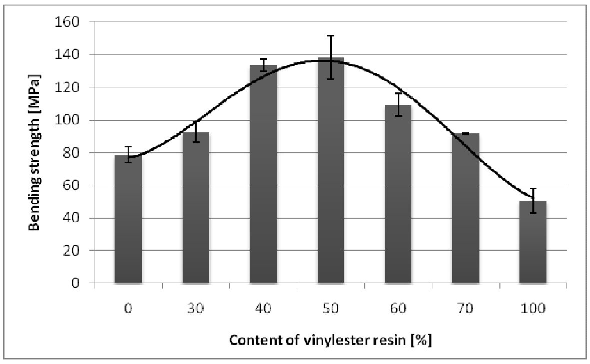

Fig. 3. Bending strengths for E6/2MM epoxy-vinylester composites

Rys. 3. Wytrzymałość na zginanie kompozytów epoksydowo-winyloestrowych E6/2MM

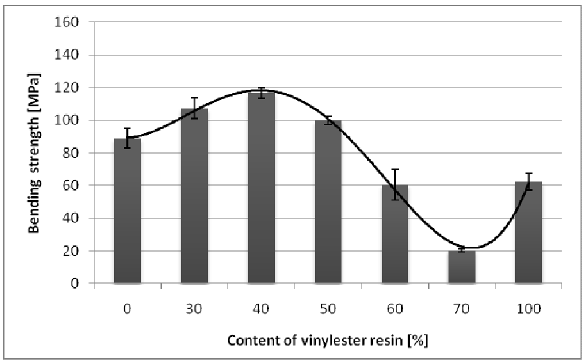

Fig. 4. Bending strengths for AM22/AT epoxy-vinylester composites

Rys. 4. Wytrzymałość na zginanie kompozytów epoksydowo-winyloestrowych AM22/AT

The tensile strengths of the hardened epoxy-vinylester compositions are generally higher than the composites based on epoxy or vinylester resin.

The research leads to the conclusion that a definite optimum of vinylester resin content exists, for which maximum bending strength is reached.

In the case of the compositions with Epidian 6 and VE-2MM (Fig. 3), higher mechanical strengths were observed in a wider range of vinylester resin content (from 30 to 70 wt.%.). For the composites obtained from Ampreg 22 and Atlac 580 ACT (Fig. 4) higher or comparable values of this parameter were obtained for composites with 30 to 50 wt.%. contents of vinylester resin. The same tendency was observed for tensile strengths for the materials described.

Thermal properties - Glass transition temperature

The values of the glass transition temperature of epoxy-vinylester composites obtained by means of the DMTA method are shown in Table 5.

TABLE 5. **Glass transition temperature for epoxy-vinylester composites**
TABELA 5. **Temperatura zeszklenia kompozytów epoksydowo-winyloestrowych**

No.	Epoxy resin	Vinylester resin	Content of vinylester resin %	Glass transition *Tg* °C
1	E6	-	0	129.5
2	E6	2MM	30	103.5
3	E6	2MM	40	105.0
4	E6	2MM	50	103.0
5	E6	2MM	60	107.5
6	E6	2MM	70	98.0
7	-	2MM	100	127.5
8	AM22	-	0	98.0
9	AM22	AT	30	86.2
10	AM22	AT	40	93.5
11	AM22	AT	50	73.5
12	AM22	AT	60	74.0
13	AM22	AT	70	86.4
14	-	AT	100	131.5

For the studied materials which consisted of independent polymer matrices, only one glass transition can be observed, which leads to the conclusion that in this case Simultaneous Interpenetrating Networks - SIN were obtained.

CONCLUSION

Introducing vinylester resin to epoxy resin decreases the viscosity of an uncured composition [6]. This modification fosters the obtaining of a finished product. Moreover, the prices of vinylester resin are lower than for epoxy resin, therefore using epoxy-vinylester resin decreases the price of the finished product, and by means of a proper curing process and optimum vinylester content, its mechanical properties are improved.

The results obtained for two epoxy-vinylester systems lead to the statement that an interpenetrating polymer network was formed by using 1-ethylimidazole and t-butyl perhydroxide as curing agents.

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