Optimization of the rheological properties of epoxy resins for glass and carbon reinforced plastics

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Abstract. Vacuum assisted resin transfer moulding (VARTM) offers advantages such as simplicity, low cost of consumables, and the ability to carry out the impregnation process and curing without using expensive equipment and tooling. In the VARTM process, rheological properties of resin have a critical impact on the impregnation and curing process. In this article, the experimental results of viscosity are presented, including the glass transition temperature, and the tensile and bending strength of the epoxy binders with the amine hardener, which depend on the quantity of its active solvent composition. The active solvent used is diethylene glycol. It shows that for an increase in the content of the active solvent, a reduction in the viscosity and a reduction of the glass transition temperature and strength occurs. The optimum composition of the binder is selected by using the Pareto optimization criteria and the Cayley–Smorodinskaya method. By using the epoxy binder, the active solvent should not exceed 10-15% by weight. This approach helps to optimize the amount of active solvent added to the epoxy resins for the criterion of viscosity, strength, and heat resistance.

1. Introduction
Fibreglass and carbon reinforced plastic composite materials are widely used in various industries, including aerospace, aeronautics, automotive, marine and others [1]. Different types of pre-preg are traditionally used to form a composite structure; however, there are many disadvantages such as the expense of the technology and limited viability of pre-preg for small-scale production.

In recent years, different types of composite moulding process are widely used in the composite industries. Among them, vacuum Assisted Resin Transfer Moulding (VARTM), also referred to as infusion, has been developed as a variant of the traditional Resin Transfer Moulding (RTM) process to reduce the cost and design difficulties and to eliminate the pre-preg requirements for composite structure. In VARTM, the upper half of a conventional mould is replaced by a vacuum bag. This eliminates the need for making a precisely matched metal mould as in the conventional RTM process. The resin dampens the fibre, and the part is then cured inside the mould.

The main advantages of infusion technology are simplicity, low cost of consumables, the ability to carry out the impregnation process and curing without the use of expensive equipment and tooling.

The speed of the impregnation process is determined by the properties of the binder and woven fibre; however, in practice problems arise often when the designer is given the specific type of woven fabric. In this situation, all the properties of the given carbon woven fabric were taken account while choosing the binder.
The most widely used binders in the manufacturing of carbon fibre reinforced plastic structure are epoxy binders. The advantages of epoxy resin are good adhesion, high mechanical properties, low shrinkage and very good processing properties. The main technological disadvantage of epoxy resins is very high viscosity.

Various additives are used in the composition of epoxy resin to reduce the viscosity. Among them, active solvents are the most widely used as an additive; however, this leads to a reduction of heat resistance and a reduction of mechanical strength while adding the active solvent in composition to improve the dampening characteristic and rheological properties of other binders [2].

The aim of this work is to optimize the active solvent content in the epoxy resins for the criterion of viscosity, strength, and heat resistance.

2. Theoretical approach
A variety of indicators can be used as optimality criterion “\( h \)”. In general, the optimality condition has the form

\[
h_1(x') < h_1(x'') = x' \succ X x'',
\]

\[
h_2(x') > h_2(x'') = x' \succ X x'',
\]

where \( h_1 \) and \( h_2 \) are two criteria that characterize the properties of the object of study; \( X \) is the solution set obtained; \( x' \) and \( x'' \) are solutions for first and second criteria; and \( \succ \) indicates a preference for solution \( x' \) compared with solution \( x'' \) in the set \( X \).

As a result, from the equation (1), the impregnation process is better and faster for smaller values of criterion \( h_1 \), and on the other hand, a higher value of criterion \( h_2 \) leads to better properties.

It is proposed to use \( h_1 \) as a criterion of the binder viscosity index, because the lower the viscosity, the quicker and more accurately the pass process impregnates the woven fabrics.

As a criterion for \( h_2 (h_3, h_4, \text{etc.}) \) a variety of indicators may be used, such as the glass transition temperature (\( h_2 \)), bending strength (\( h_3 \)) and the tensile stress (\( h_4 \)).

When using the multiple criteria, a correlation must be established between them using the correlation coefficient \( r \). The correlation coefficient \( r \) is defined as follows

\[
r_{1,2} = \frac{I_{1,2} - I_1 I_2}{\sqrt{(I_{1,1} - I_1^2)(I_{2,2} - I_2^2)}}
\]

\[
I_1 \equiv \frac{1}{N} \sum_{i=1}^{N} h_1(A_i)
\]

\[
I_{1,2} \equiv \frac{1}{N} \sum_{i=1}^{N} h_1(A_i) h_2(A_i)
\]

where \( r_{1,2} \) is the correlation coefficient for criteria numbered 1 and 2; and \( A_i \) is the point in the area of parameters to be optimized.

3. Experimental approach
In this study, the properties of 8 epoxy binder compositions, each with different levels of active solvent content are investigated experimentally. Results are shown in table 1. The active solvent used is diethylene glycol (DEG).

After adding different amounts of active solvent, the viscosities of the binders were determined by Brookfield viscometer CAP-2000. The glass transition temperature was evaluated by differential scanning calorimetry, DSC 204 F1. These binders were filled in standard forms (GOST 12015) and
after curing were tested for tensile (GOST 11262) and bending strength (GOST 4648). The experimental results for viscosity, glass transition temperature, tensile and bending strength are shown in table 2.

### Table 1. Different diethylene glycol compositions of epoxy binder

| Binder composition | Active solvent DEG content (% by weight) |
|--------------------|------------------------------------------|
| 1                  | 0                                        |
| 2                  | 1                                        |
| 3                  | 5                                        |
| 4                  | 10                                       |
| 5                  | 15                                       |
| 6                  | 20                                       |
| 7                  | 25                                       |
| 8                  | 30                                       |

### Table 2. Properties of the binders

| Binder composition | Viscosity (Pa s) | Glass transition temperature (°C) | Max. Tensile strength (MPa) | Max. Bending strength (MPa) |
|--------------------|------------------|----------------------------------|-----------------------------|-----------------------------|
| 1                  | 17               | 61                               | 109                         | 139                         |
| 2                  | 12.5             | 61                               | 105                         | 143                         |
| 3                  | 3.6              | 58                               | 90                          | 145                         |
| 4                  | 1.15             | 58                               | 90                          | 148                         |
| 5                  | 0.86             | 58                               | 85                          | 115                         |
| 6                  | 0.54             | 56                               | 83                          | 107                         |
| 7                  | 0.27             | 56                               | 85                          | 110                         |
| 8                  | 0.18             | 56                               | 85                          | 107                         |

### Table 3 The values of correlation coefficients

| Criteria                      | The values of the correlation coefficient |
|-------------------------------|--------------------------------------------|
| Active solvent content - Viscosity | 0.7861                                     |
| Active solvent content - glass transition temperature | 0.9091                                     |
| Active solvent content - destructive bending stress | 0.8734                                     |
| Active solvent content - destructive tensile stress | 0.8164                                     |
| Glass transition temperature - Bending and tensile strength | 0.9439                                     |

### 4. Results and discussion

Using equation (2) and the results in table 2, the correlation coefficients were determined, as shown in table 3.

Analysis of the values of correlation coefficients in table 3 show that the highest one is the criteria of the glass transition temperature – bending and tensile strength. This means that the increasing binder active solvent content leads to a decrease in the glass transition temperature and reduction in bending and tensile strength.
Since the viscosity reduction is a positive factor, this value can be directly included as one of the criteria for solving the optimization problem in terms of minimization.

The glass transition temperature is the second criterion for evaluating the effectiveness of the increase of active solvent content. Lowering this value has a negative impact because it reduces the operating temperature range.

Using the relative characteristics, optimality criterion changes are

\[ h_2 = \Delta h_2 = h_{2\text{max}} - h_2 \]  

(3)

The correlation coefficient of this pair is 0.9154, which could be assigned to the class of multi-criteria optimization problem [3].

Figure 1. Dependence of normalized criteria on the viscosity and glass transition temperature drop

According to the Pareto criterion, optimization approach of the resin composition is

\[ x', x^* \in X, h_i(x') \leq h_i(x^*), i = 1, \ldots, m \]

\[ \exists k \in \{1, 2, \ldots, m\} : h_k(x') < h_k(x^*) = x' \succ^*_x x^* \]  

(4)

The test criteria were further normalized,

\[ h_{1n} = h_1 / h_{1\text{max}} \]

\[ h_{2n} = (h_{2\text{max}} - h_2) / h_{2\text{max}} \]  

(5)
The dependence of the normalized criteria is presented in figure 1. The points illustrate different binder variants.

![Figure 1](image)

**Figure 2.** Dependence of the normalized criteria on the viscosity and glass transition temperature on the characteristics of active solvent

To obtain a unique solution, randomized strategies were used based on the information about the relative importance of criteria [4]. When choosing the optimal solution, the theorem of the vector criterion is used with weight coefficients \( \{\alpha_i\} \). The corresponding generalized criterion calculated by the formula is thus

\[
J(x, \alpha) = \langle h(x), \alpha \rangle = \sum_{i=1}^{m} \alpha_i h_i
\]  

where \( \alpha = (\alpha_1, \ldots, \alpha_m) \) – vector of non-negative weight coefficient satisfies the equation,

\[
\sum_{i=1}^{m} \alpha_i = 1
\]  

As shown in figure 1, the points illustrate the different binder variants in table 1, which correspond to the values of the normalized viscosity. The normalized criteria of viscosity and glass transition temperature for different values of the weight coefficients is shown in figure 2.

Three weight coefficient values are presented in figure 2 with different colours, and the optimum compositions are compositions 4 and 5, i.e. DEG compositions of 10 or 15%.

Verification of the result was conducted using the theory of cooperative games [5]. For this optimization approach, the initial data was set at the maximum allowable values for each variable. The Cayley - Smorodinskaya solution is shown in figure 3.
As follows from the data obtained, the optimum compositions are compositions 4 and 5, which corresponds to the previous solution.

5. Conclusions
The study shows the influence of the content of epoxy binder active solvent on viscosity change, glass transition temperature and mechanical properties after curing. It has been determined that by increasing the content of active solvent in the binder there is decrease of viscosity, which has a positive effect on the entire process of manufacturing the product; however, this method of viscosity reduction results in deterioration of heat resistance and mechanical strength. By using the Pareto optimization criteria, the best epoxy binder compositions were predicted to be those with DEG composition of 10 or 15%.

References
[1] Baurova N 2013 Microstructural Investigations of Surfaces of Destruction of Carbon Plastic Polymer Science - Series D. 6(2) 246–249
[2] Malysheva G, Akhmetova E and Marycheva A 2014 Estimation of glass transition temperature of poly sulfone -modified epoxy binders Glass Physics and Chemistry 40(5) 543–548
[3] Lotov A and Pospelov I 2008 Multicriteria decision making problems (Moscow: Moscow State University Press)
[4] Chernorutsky I 2005 Methods of decision-making (S.Publishing House of Petersburg)
[5] Шварц ДТ 2013 Интерактивные методы решения задачи многокритериальной оптимизации. Обзор. Наука и образование. Электронный журнал 4 [Schwartz DT 2013 Interactive methods of solving the problem of multi-criteria optimization. Overview. Science and education. Electronic journal, in Russian]