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INFLUENCE OF HEAT PRETREATMENT ON CROSS-LINKING BEHAVIOR AND THERMAL PROPERTIES OF THERMOSET SEMI-FINISHED PRODUCTS WITH POWDER RESIN SYSTEMS

The aim of this work was to determine the influence of thermal pretreatment of thermoset semi-finished products on the thermal properties as well as the subsequent processing parameters. For this purpose, the curing behavior in the pretreatment of thermoset fiber reinforced semi-finished products was analyzed. A semi-finished product with glass fiber reinforcement and powder resin system A.S.SET 1010 was investigated. During processing of the rigid semi-finished products, melting-up of the matrix system is necessary before shaping. To determine the influence of this process, samples were pretreated and tested at different heating temperatures and times. The change in the glass transition temperature and the degree of cross-linking was determined using thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC). Thanks to this, the curing behavior and thermal properties of the semi-finished products were evaluated during their pretreatment depending on the heating temperature and time. It was confirmed that the pretreatment has a major influence on the degree of cross-linking, glass transition temperature as well as the later processing parameters.

Keywords: thermosets, powder processing, glass fibres, thermal properties

WPŁYW CHARAKTERYSTYKI TEMPERATUROWEJ PROCESU TECHNOLOGICZNEGO NA PRZEBIEG SIECIOWANIA ORAZ WŁASNOŚCI TERMICZNE PÓLFABRYKATÓW ZE SPROSZKOWANEJ ŻYWICY EPOKSYDOWEJ

Celem pracy było wyznaczenie wpływu wstępnej obróbki cieplnej na właściwości termiczne włóknistych półproduktów na bazie termoutwardzalnych polimerów, a także na późniejsze parametry przetwórcze. W tym celu wyznaczona została charakterystyka sieciowania półproduktów w trakcie wstępnej obróbki termicznej. Analizowane półprodukty składały się z tekstylnego wzmocnienia z włókna szklanego oraz sproszkowanej żywicy epoksydowej A.S.SET 1010. Proces przetwórczy włóknistych półproduktów na bazie sproszkowanej żywicy epoksydowej wymaga stopienia materiału osnowy w celu umożliwienia formowania struktur trójwymiarowych. W celu wyznaczenia wpływu tego procesu przygotowane próbki zostały wstępnie poddane obróbce termicznej z różnymi charakterystykami procesu nagrzewania. Zmiany w temperaturze zeszklenia, jak również stopniu usieciowania zostały wyznaczone za pomocą analizy termogravimetrycznej (TGA) i różnicowej kalorymetrii skaningowej (DSC). Dzięki temu została wyznaczona zarówno charakterystyka procesu sieciowania, jak i zmiana właściwości termicznych półproduktów na bazie sproszkowanej żywicy epoksydowej w trakcie wstępnej obróbki cieplnej w zależności od temperatury i czasu nagrzewania. Potwierdzono również znaczący wpływ obróbki cieplnej na stopień usieciowania, temperaturę zeszklenia i parametry procesu przetwórczego.

Słowa kluczowe: właściwości termiczne, proces proszkowy, włókno szklane

INTRODUCTION

The use of structural lightweight materials, in particular fiber-reinforced plastics (FRP), leads to significant savings of energy, raw materials and costs [1-4]. In the case of fiber-plastic composites, the fiber and matrix components assume various tasks. The low-density plastic matrix surrounds the fibers and protects them against external influences. Without it, the high specific strengths and stiffness of the fibers could not be utilized. The fiber characteristics, infiltration quality, fiber matrix adhesion and thermomechanical properties

of the matrix material are relevant for the properties of FRP. Especially, thermosetting materials, due to their three-dimensionally cross-linked molecular structure, have high mechanical properties, good thermal stability and are comparatively resistant to external chemical influences [2, 4].

However, manufacturing FRP components with thermoset matrices is usually complex and cost-intensive. Therefore large-scale production processing is still restricted. Many fiber-reinforced thermosets, including

some snap-cure epoxy resins, are cured under elevated temperatures. The reason for this is increased cross-linking of the molecular chains, as a result of which the laminate quality as well as the mechanical and thermal properties are improved [5].

A.S.SET belongs to the systems mentioned above since the powder is solid at room temperature, must be melted for processing and is consolidated under increased temperature. In order to process A.S.SET, it is important to know the thermal properties of the resin system. During the manufacturing process, the A.S.SET material is pre-heated and the molecules begin to cross-link. Depending on the heat supply, a certain degree of pre-cross-linking occurs during the pretreatment. In this study, the influence of thermal preheating on the glass transition temperature, pre-cross-linking degrees and processing properties were investigated using differential scanning calorimetry (DSC) and thermogravimetry (TGA). Thus, conclusions about the structural changes in the resin during processing were made. Thanks to these investigations, it is possible to find suitable parameters for heat pretreatment for production optimization in order to achieve the lowest possible cycle times [6-8].

MATERIALS

Within this study, pure resin samples as well as fiber reinforced semi-finished products were investigated. Therefore, the epoxy powder resin A.S.SET 1010 (New Era Materials) and A.S.SET SHEETs (New Era Materials) were considered. The reinforcement and the matrix material in the semi-finished product were one layer of a unidirectional glass fabric (220 g/m², 92145 Inter-glass) and epoxy powder resin A.S.SET 1010 respectively. The thickness of the A.S.SET SHEETs was 0.3 mm. The fiber mass fraction of the semi-finished product was 35%.

METHODS

Preparation of specimens

In order to investigate the influence of heat pretreatment on the cross-linking degree of the semi-

finished products, the samples were prepared under process-specific conditions.

For this purpose, 100 mm x 50 mm samples were cut from a UD-A.S.SET SHEET and heated using a heating plate. The sample numbers, heating time and heating temperature are shown in Table 1.

In addition to the heat-treated A.S.SET SHEETs (1-23), untreated A.S.SET 1010 resin (26), fully-cured A.S.SET 1010 resin (25) and untreated A.S.SET SHEET (24) were also examined. Since the matrix material is heated to a certain temperature during production of the A.S.SET SHEET, specimen 24 serves as a reference for the heat-treated specimens.

The manufacturing process of components using A.S.SET SHEETs is performed by preheating one side of the A.S.SET SHEET [9]. According to this, heat treatment of the specimens was also carried out on one side at this point. For this purpose, the heating plate was covered with PTFE film. Since the film has an insulating effect, temperature sensors were used to determine the exact surface temperature of the film. A.S.SET SHEETs were placed on the film and fixed with a PTFE piece. This ensured that there was no air gap between the heating plate and foil, nor between the foil and sheet, and the sheets experienced the same temperature as the sensors. The experimental setup is shown in Figure 1.

TABLE 1. Details about investigated specimens
TABELA 1. Szczegółowe informacje dotyczące badanych próbek

Temperature [°C]	Time <i>t_w</i> [s]							
			10	30	50	70	90	900
	26 ¹⁾							
		24 ²⁾						
80			1	2	3	4	5	
90			6	7	8	9	10	
100			11	12	13	14	15	
110			16	17	18	19	20	
120			21	22	23			25 ³⁾
Untreated A.S.SET resin								1)
Untreated A.S.SET SHEET								2)
Cured A.S.SET resin								3)

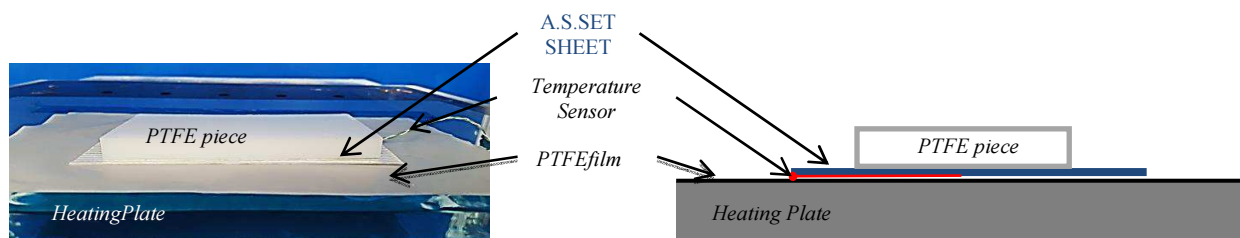


Fig. 1. Experimental setup for heat treatment of specimens
Rys. 1. Stanowisko do wstępnej obróbki cieplnej próbek

In the experiments, at 120°C strong brown coloration of the sheets could be observed even at dwelling times t_w as low as 30 and 50 seconds. Therefore tests were not carried out at 70 and 90 seconds.

Thermogravimetry (TGA)

Thermogravimetric analyses (TGA) were performed to determine the exact matrix mass of the samples in order to estimate their cross-linking enthalpy. On the basis of the preliminary tests a heating rate of 10 K/min was selected, in the temperature range of 25°C to 500°C under nitrogen and air atmosphere. The conditions were held constant (isothermal at 500°C) for 90 minutes [10]. With these parameters, the mass loss of the pure powder was more than 98% and further a mass reduction was not measurable at 500°C for 20 minutes.

Differential scanning calorimetry (DSC)

The thermal properties of the specimens were determined by differential scanning calorimetry (DSC) in the temperature range of 20 to 200°C, at a heating and cooling rate of 10°C/min under air atmosphere. The temperature accuracy of the measuring instrument was $\pm 0.2^\circ\text{C}$ and the heat flow had a resolution of 0.04 μW . First, the melting process was considered, glass transition temperature T_g and reaction enthalpy H_{ges} of the entire sample (fibers and matrix) were determined. Furthermore, cross-linking degree χ of the heat-treated specimens was calculated from cross-linking enthalpy (based on the matrix mass) H_{Matrix} . A connection between the heat treatment and the degree of cross-linking was determined with the obtained values.

RESULTS

Determining matrix mass

The TGA yielded a significant mass loss for all the samples. In the case of the pure resin samples (25 and 26), the mass loss averaged 98.45%. This means, that about 98.45% of the matrix mass is decomposed during the analyses. In order to obtain the most accurate results possible, the determined matrix masses m_{Matrix} are calculated according to Equation (1):

$$m_{Matrix} = \frac{m_{Matrix}(TGA)}{98.45\%} \cdot 100\% \quad (1)$$

For the A.S.SET SHEET specimens (1-24), the mass fraction of the matrix was between 23% and 55%. Partly very low matrix mass fractions were caused by the fact that the matrix powder partially precipitated during sample preparation. Furthermore, during the heat pretreatment, molten resin residues remained adhered to the PTFE film, whereby the matrix mass fraction was additionally reduced.

Determining glass transition temperature

In order to determine the influence of the heat treatment on the thermal properties and the degree of cross-linking of A.S.SET SHEETS, the test was carried out according to the ASTM E1356 standard [11].

The glass transition temperature was determined for all the samples. For some samples, the DSC analysis was repeated since the determined glass transition temperatures were considerably different from the expected values. Table 2 shows the glass transition temperatures relevant for the evaluation.

TABLE 2. Evolution of glass transition temperatures of specimens after heat pretreatment

TABELA 2. Zmiany temperatury zeszklenia próbek po obróbce cieplnej

Temperature [°C]	Time [s]							
			10	30	50	70	90	900
	39.54 ¹⁾							
		40.91 ²⁾						
80			45.93	44.87	45.80	45.48	47.14	
90			44.76	45.07	45.70	47.38	48.34	
100			44.49	47.02	47.25	48.27	49.64	
110			44.72	48.41	50.76	51.55	53.19	
120			50.24	52.09	58.29			115.48 ³⁾

The glass transition temperature increases as expected with an increasing heat input, which indicates an increment of the cross-linking degree. The untreated powder, which has not yet received any heat, has a glass transition temperature of 39.5°C. The non-heat-treated A.S.SET SHEET, which has been exposed to an elevated temperature during manufacturing for a very short time, has a slightly increased glass transition temperature of 40.9°C. The fully cured resin has a glass transition temperature of 115.5°C. Since the glass transition does not take place at an exact temperature but in a temperature range, deviations of $\pm 2^\circ\text{C}$ have to be added to the temperatures listed in Table 2. Additionally, Figure 2 shows the results of the measurements of the glass transition temperatures.

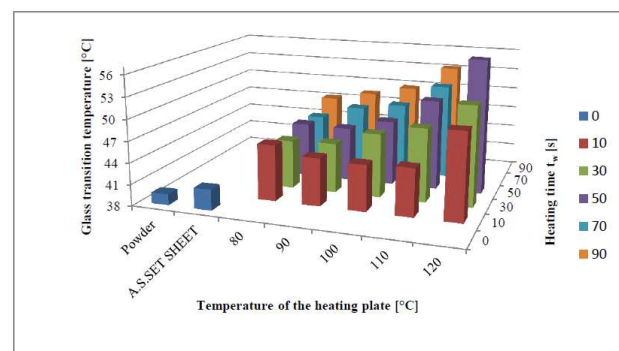


Fig. 2. Evaluation of glass transition temperatures of specimens after heat pretreatment

Rys. 2. Zmiany temperatury zeszklenia próbek po obróbce cieplnej

Determining cross-linking degree according to reaction enthalpy

In the next step, the heat energy (reaction enthalpy) for the entire sample, H_{ges} , from the peak area of the DSC curve was determined. Specific cross-linking enthalpies H_{Matrix} were determined for each sample according to Equation (2):

$$H_{Matrix} = \frac{H_{ges}}{m_{Matrix}} \quad (2)$$

With an increasing heat supply, the released cross-linking enthalpy H_{Matrix} decreases, which indicates an increased cross-linking degree of the sample. The cross-linking degree of the heat-treated samples was calculated by means of the specific cross-linking enthalpy. It was assumed that the pure A-S-SET POWDER 1010 (resin) has a cross-linking degree of 0%. The degree of cross-linking χ of the samples was calculated according to Equation (3) and is shown in Table 3. The compiled results concerning the cross-linking degree are depicted in Figure 3.

$$\chi = \frac{H_{Matrix}(resin) - H_{Matrix}(specimen)}{H_{Matrix}(resin)} \cdot 100\% \quad (3)$$

TABLE 3. Evolution of cross-linking degree χ [%] of specimens after heat pretreatment

TABELA 3. Zmiany stopnia usieciowania χ [%] próbek po obróbce cieplnej

Temperature [°C]	Time [s]							
		10	30	50	70	90	900	
	0 ¹⁾							
		2.3 ²⁾						
80		18.5	42.8	2.7	0.8	2.8		
90		5.8	6.4	8.7	9.1	18.7		
100		5.1	12.4	-	17.6	27.5		
110		16.3	11.2	29.4	38.4	48.7		
120		8.9	52.6	48.1			97.4 ³⁾	

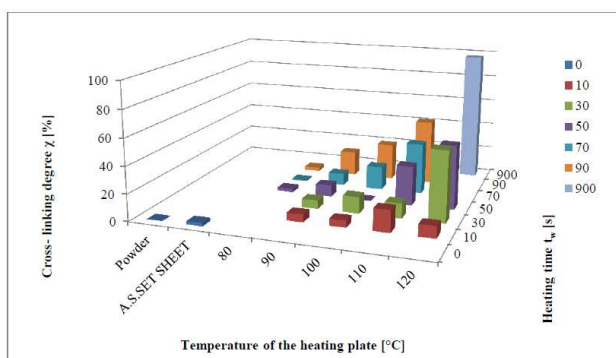


Fig. 3. Evaluation of cross-linking degree of specimens after heat pretreatment

Rys. 3. Zmiany stopnia usieciowania próbek po obróbce cieplnej

The cross-linking degree of the sheets increases with an increasing temperature and duration time of heat treatment. Assuming that the cross-linking degree of the powder is 0%, a cross-linking degree of 2.3% was determined for the untreated A.S.SET SHEET. The

cured A.S.SET material had a cross-linking degree of 97.4% after 15 minutes at 120°C.

The specific cross-linking degrees were plotted over the time of heat treatment in a graph (Fig. 4). A curve was determined for each temperature. The evaluation indicates a linear relationship (Eq. (4)) between cross-linking degree χ and duration t_w of the heat treatment. Only at 120°C is the scattering is very high, which was caused by the high acceleration of the curing reaction. In addition, it was not possible to have immediate cooling of the sample after the heat pretreatment, which additionally influenced the cross-linking degree.

$$\chi(t_w) = \frac{\partial \chi}{\partial t_w} \cdot t_w \quad (4)$$

The intersection point of the straight line was chosen so that a cross-linking degree of 0% was assumed at 0 seconds.

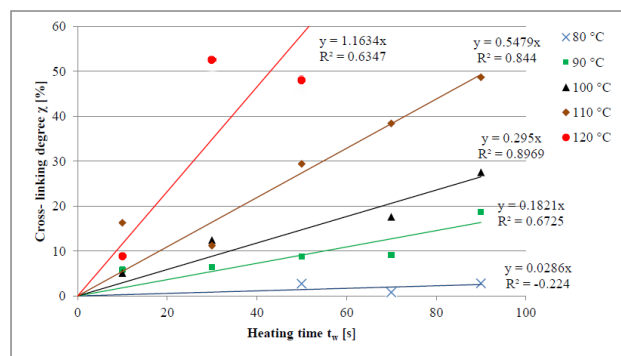


Fig. 4. Extrapolation of cross-linking curves $\chi(t_w)$

Rys. 4. Charakterystyka sieciowania w zależności od temperatury oraz czasu nagrzewania

A rising slope of the curve with increasing heating temperature can be observed. In Table 5, the ascertained regression coefficients are listed as a function of temperature and heating time. They can be used to determine the actual degree of cross-linking of the semi-finished products and adaptation of the subsequent processing parameters.

TABLE 4. Estimated regression coefficients depending on temperature and heating time

TABELA 4. Wyznaczone współczynniki zmiany stopnia usieciowania w zależności od temperatury oraz czasu nagrzewania

Temperature [°C]	Slope of function [-]
80	0.0286
90	0.1821
100	0.295
110	0.5479
120	1.1634

CONCLUSIONS

The pre-heating of the semi-finished products has a significant influence on the resulting properties as

well as processing parameters. The investigations have shown that during the heating process, the curing reaction is accelerated. This can be clearly seen by observing the determined specific glass transition temperature as well as the cross-linking degree of the semi-finished products. Compared to the untreated sheets, a significant increase in the cross-linking degree was observed even at low temperatures and at a short heating time. Moreover, the connection between the temperatures, heating time and cross-linking degree was monitored.

The obtained results are very advantageous concerning characterizations of the investigated material combinations and can be used to increase the efficiency in the production of composite components with snap-cure resin systems.

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