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EFFECT OF GLASS FIBRE PRESENCE ON CURING PROCESS OF UNSATURATED POLYESTER RESIN

The paper presents an attempt to estimate the difference in the intensity of the curing process of a polyester resin: without any filler and filled with fragmented glass fabric. Curing of the resin samples was carried out at room temperature. The temperature-time course of the process and gel time were recorded for each sample. On the basis of the obtained results and the conducted observations, it was found that filling the resin with fragmented glass fabric caused a decrease in the peak temperature of the curing process and increased the time of reaching this temperature. These effects were found to intensify with an increase in filler weight (inhibitory effect of the filler). A slightly longer gelation time was also found for the filled resin in comparison to the unfilled one. The observed effects indicate an increase in the thermal insulation of the curing mass along with an increase in filler content. They also indicate that the presence of fibers leads to stabilization (improvement of repeatability) of the resin curing process. The work is a continuation of earlier work aimed at experimental evaluation of the behavior of curing resins, which in turn will help to systematize the practical knowledge in this field. Thus, it finally meets the expectations of users and processors of curable resins.

Keywords: curable resin, curing process

WPŁYW OBECNOŚCI WŁÓKIEN SZKLANYCH NA PRZEBIEG SIECIOWANIA ŻYWICY POLIESTROWEJ

Zaprezentowano próbę oszacowanie różnicy w intensywności procesu sieciowania żywicy poliestrowej bez żadnego napełniacza oraz napełnionej rozdrobnioną tkaniną szklaną. Utwardzanie próbek żywicy prowadzono w temperaturze pokojowej i rejestrowano przebieg temperaturowo-czasowy procesu oraz czas żelowania. Na podstawie uzyskanych wyników i poczynionych obserwacji stwierdzono, że napełnienie żywicy rozdrobnioną tkaniną szklaną spowodowało zmniejszenie temperatury szczytu procesu utwardzania oraz wydłużyło czas osiągania tej temperatury. Stwierdzono postępowanie tych efektów ze zwiększeniem masy napełniacza (inhibicyjne działanie napełniacza). Dla żywicy napełnionej stwierdzono też nieznaczne wydłużenie czasu żelowania. Zaobserwowane efekty wskazują na zwiększenie izolacyjności termicznej sieciującej masy wraz ze wzrostem zawartości napełniacza. Wskazują też, że obecność włókien prowadzi do stabilizacji (poprawy powtarzalności) procesu sieciowania żywicy. Praca jest kontynuacją wcześniejszych prac, mających na celu eksperymentalną ocenę zachowania się utwardzanej żywicy, co z kolei pomoże usystematyzować praktyczną wiedzę w tym zakresie i wyjść naprzeciw oczekiwaniom użytkowników oraz przetwórców żywic utwardzalnych.

Słowa kluczowe: żywica utwardzalna, proces utwardzania

INTRODUCTION

The problem of curing of curable resins is one of the main issues related to the processing of this group of materials, including the technology of polymer-matrix composites. It is a complex problem because the course of the resin curing process depends on many factors (ambient temperature, quality and quantity of catalysts, volume of the cured portion, heat removal from the curing area) [1-4]. Meanwhile, the intensity of the curing process is very important for the final quality and performance of the cured resin [1, 5]. An example is the quality of the obtained laminate surface, which strongly depends on the course of resin curing [4, 5]. Precise data on the course of resin curing are rarely taken into account when designing the process of manufacturing products containing resins [4, 6, 7]. However, it is highly probable that the course of resin curing has an impact on problems related to the technology of manufacturing various products, e.g. errors in the modeling of laminate pressure forming processes [8-10].

Curing polyester resin with styrene is an exothermic process that is simultaneously heat-activated [3, 11]. The course of the process depends significantly on the volume of the hardened sample due to the influence of the insulating properties of the mass being cured on the internal heat distribution and the temperature level [1, 4, 12]. Curing of the resin containing filler signifi-

cantly changes the process conditions in comparison to the neat resin. The presence of a material with a certain thermal capacity that receives part of the heat of the curing reaction obviously affects the process. This has been analyzed, for example, in hot pressing conditions (contribution of elevated temperature and pressure) [13]. The fundamentality of the influence of the solid phase on the behavior of the surrounding liquids was found for numerous liquid phase processes [14-19]. In the case of curable resins, the problem of the impact of the solid phase on the course of the curing process has not been satisfactorily demonstrated in the literature. Moreover, due to its importance it should be treated as a separate model issue. The authors decided to initiate a new approach to this problem as part of this study.

The article presents the results of research being a continuation of previous analyses of curing polyester resin of different volumes [1]. Its aim is to show and estimate the differences in the intensity of the resin curing process (by comparing the temperature-time relation and gelation time) at room temperature, without any filler (neat) and filled with fragmented glass fabric.

MATERIALS AND METHODS

The curing tests were carried out using polyester resin ESTROMAL 14 LM with the METOX 50 catalyst added in the amount of 4% by weight.

The filler used was KROSGLASS glass fabric (320 g/m^2) mechanically fragmented into pieces with a diameter not exceeding 3 cm (Fig. 1a).

Fig. 1. Realization of resin curing tests: a) pieces of fragmented glass fabric, b) samples of fabric pieces in measuring vessels, c) curing tests - visible sample with pieces of fabric and neat resin sample, thermocouples also visible placed under surface mirror of curing resin

Rys. 1. Realizacja prób sieciowania żywicy: a) kawałki rozdrobnionej tkaniny szklanej, b) próbki kawałków tkaniny w naczyniach pomiarowych, c) próby sieciowania - widoczna próbka z kawałkami tkaniny oraz próbka nite, widoczne też termopary wprowadzone pod lustro sieciującej żywicy

The sample was prepared by introducing the prepared pieces of fabric in a glass measuring vessel (all the vessels used were of the same dimensions), in the amount weighed to the nearest 0.1 g. Two groups of 3 samples were prepared. One group contained 70 g of the fabric fragments, the other one containing 35 g (Fig. 1b). For each prepared sample, an empty glass vessel was prepared for simultaneous curing of an equivalent neat resin sample.

The tests were started by mixing the resin with the catalyst in a separate vessel (150 g resin + 6 g catalyst) and filling the measuring vessels - one filled with pieces of fabric and one empty one. The resin was mixed vigorously with the pieces of fabric for 60 seconds. At the same time, the neat resin sample was also intensively mixed to ensure repeatability of the curing process conditions.

After mixing the resin in the vessels, thermocouples were inserted into them, fixed on supports (Fig. 1c) and fixed in position. Each thermocouple tip was in the center of the surface mirror and in the middle of the height of the curing mass column. Thermocouple temperature measurement was started 60 seconds after the end of mixing (frequency 1 Hz) and the pyrometer was used to measure the surface temperature. Subsequent measurements by the pyrometer were performed every 1-5 minutes, and during the intensive stage of the crosslinking process, every 10 seconds. A K-type thermocouple (Chromel/Alumel) was used with a CZAKI TP-202K-1b-500-1.0 sensor of a range from –20 to +9000°C, a CRYSTALDIGRAPH 8T recorder and a FLUKE 62 MAX + pyrometer. The room temperature was 18°C.

During the temperature measurements, viscosity control of the curing resin samples was carried out. This was done by sinking a rigid rod into the curing mass, pulling it out (the frequency of this activity at the intensive curing stage was 0.1 Hz) and observing the drawn threads. If the length of the continuous thread pulled from the mass was about 2 cm, the corresponding time was considered as the gelation time of the resin. This methodology was inspired by the one described in the PN-87/C-89085.19 standard for epoxy resins.

RESULTS AND DISCUSSION

As a result of the measurement procedure, the results were obtained in the form of temperature-time curves, shown in Figures 2 and 3.

On the obtained temperature-time curves, one can clearly see that filling a polyester resin with a fragmented glass fabric affects the curing process. In the case of smaller samples (35 g) evident lowering of the curves in the area of intensive reaction can be seen. Moreover, in the case of larger samples (70 g), the curves are additionally shifted along the time axis. This is confirmed by the peak temperature (maximum temperature of the curing process) obtained for individual sample types (Tables 1 and 2).

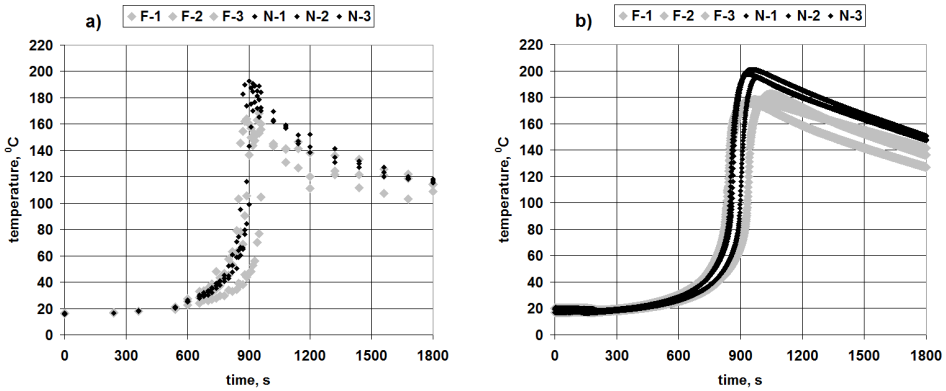

Fig. 2. Temperature-time dependence for curing process of neat polyester resin (des. N) and resin filled with 35 g of fragmented glass fabric (des. F): a) measurement with pyrometer on upper surface of sample, b) measurement with thermocouple in central point inside sample

Rys. 2. Zależność temperatura-czas dla procesu utwardzania żywicy poliestrowej nite (des. N) oraz napełnionej 35 g rozdrobnionej tkaniny szklanej (des. F): a) pomiar pirometrem na górnej powierzchni próbki, b) pomiar termoparą w centralnym punkcie wewnątrz próbki

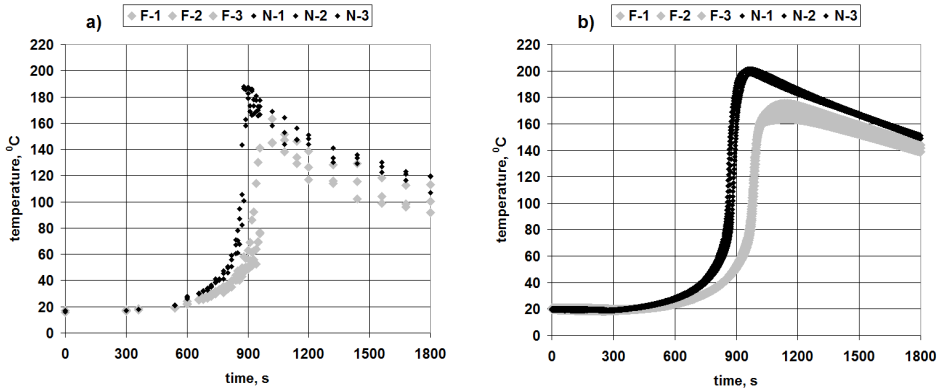

Fig. 3. Temperature-time dependence for curing process of neat polyester resin (des. N) and resin filled with 70 g of fragmented glass fabric (des. F): a) measurement with pyrometer on upper surface of sample, b) measurement with thermocouple in central point inside sample

Rys. 3. Zależność temperatura-czas dla procesu utwardzania żywicy poliestrowej nite (des. N) oraz napełnionej 70 g rozdrobnionej tkaniny szklanej (des. F): a) pomiar pirometrem na górnej powierzchni próbki, b) pomiar termoparą w centralnym punkcie wewnątrz próbki

TABLE 1. **Peak (maximum) temperature of curing process and time of its achievement - pyrometer measurement**

TABELA 1. **Temperatura szczytu (maksymalna) procesu utwardzania oraz czas jej osiągnięcia - pomiar pirometrem**

Specimen	Peak temperature [°C]	Time of reaching the peak temperature [s]
Non filled (*35)	191 (1)	917 (11)
Filled with 35 g GF	159 (10)	953 (44)
Non filled (*70)	185 (4)	893 (9)
Filled with 70 g GF	152 (8)	1040 (27)

TABLE 2. **Peak (maximum) temperature of curing process and time of its achievement - thermocouple measurement**

TABELA 2. **Temperatura szczytu (maksymalna) procesu utwardzania oraz czas jej osiągnięcia - pomiar termoparą**

Specimen	Peak temperature [°C]	Time of reaching the peak temperature [s]
Non filled (*35)	198 (2)	959 (14)
Filled with 35 g GF	179 (2)	987 (41)
Non filled (*70)	200 (1)	961 (10)
Filled with 70 g GF	170 (4)	1131 (9)

For the filled samples, both the average peak temperature decreases and the time of reaching this temperature is extended. These effects progress with an increasing mass of filling material. This means the filler has an inhibitory effect on the curing process. It also has an effect on the gelation time of the samples (Table 3).

TABLE 3. **Gelation time of polyester resin: neat one and one filled with 35 and 70 g of fragmented glass fabric**

TABELA 3. **Czas żelowania żywicy poliestrowej nite i z dodatkiem 35 oraz 70 g włókna szklanego**

Specimen	Gelation time [s]
Non filled (*35)	630 (10)
Filled with 35 g GF	660 (20)
Non filled (*70)	610 (0)
Filled with 70 g GF	625 (15)

The gelation time elongates quite evidently at 35 g (by about 5%), but at 70 g the difference is virtually irrelevant (by about 2%). The stochastic character of the gelation time should be emphasized. Determining the exact difference in gel time for the 35 and 70 g samples would require significant expansion of the sample

population. However, the obtained results can be explained by the overlap of the two effects caused by the presence of the filler: 1) a reduction in the process intensity by absorbing heat (effect - extends gelation time), 2) local heterogeneous nucleation on the surface of the fibers (effect - shortens gelation time). Apparently, in the studied case the first effect outweighs the second effect.

Attention should be drawn to the fact that the differences in peak temperatures between the unfilled and filled samples are for 35 g and for 70 g respectively: 19 and 30°C when measured by the thermocouple and 32 and 33°C when measured by the pyrometer. It means that in conditions of better heat dissipation (sample surface - pyrometer measurement), the temperature difference between the neat resin and filled resin sample is smaller than for the central area of the mass crosslinking column (thermocouple measurement), where the heat dissipation is limited by the insulating layer of the mass itself (resin or resin with fibers). This indicates an increase in the thermal insulation of the mass along with an increase in the content of glass fibers - perhaps due to an increase in the specific thermal capacity of the mass.

Additional information on the course of the curing process is provided by diagrams of the temperature-time derivative function dependence versus temperature, for the neat resin and resin filled with fragmented glass fabric (Fig. 4).

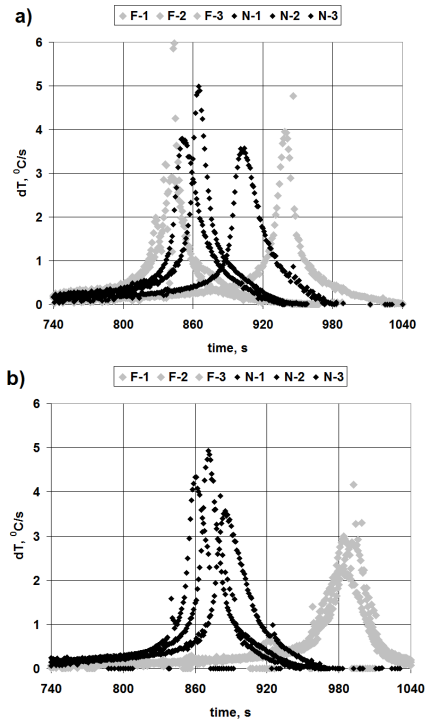

Fig. 4. Temperature-time derivative function depedence versus temperature for curing process of polyester resin: neat (des. N) and filled (des. F), thermocouple measurement: a) 35 g filling, b) 70 g filling

Rys. 4. Zależność pochodnej funkcji temperatura-czas od temperatury dla procesu utwardzania żywicy poliestrowej nite (des. N) oraz napełnionej (des. F), pomiar termoparą: a) napełnienie 35 g, b) napełnienie 70 g

The determined curves show that at the 70 g filling, the repeatability of the process is clearly better than for the neat resin - the spread of the curves is smaller (Fig. 4b). In the case of the 35 g filling (Fig. 4a), two of the three curves corresponding to the filled samples overlap, only the third is significantly shifted. Such a large displacement most probably results from external stochastic factors. In conclusion, it can be claimed on the basis of the obtained results, the presence of fibers improves the stability of the resin curing process.

As part of the study, no detailed analysis of the mechanical properties of the cured resin was carried out. Nevertheless, visual inspection of the cured samples was conducted. It was found that the neat resin samples are cracked and have a dark turbid color. The fiber-filled samples are lighter and no cracks are visible on them (of course, this may be due to the reinforcing effect of the fibers). This is in line with the previous results obtained by the authors and available in the literature. The curing of the resin in the volume occurs unevenly, which leads to stochastic distribution of the shrinkage and uncontrolled deformation as well as cracking of the resin during its crosslinking process. Local overheating of the material may also occur. This has been evidenced by the results of observations of both polyester and epoxy resin [1, 4]. Resin curing of too large a volume (e.g. products with a large cross-section) leads to significant deterioration of the mechanical properties of the cured resin and the formed composite [9]. In turn, when the curing resin contains a fiber preform, the curing is more uniform, as determined by measurements using sensors [8].

An additional observation made during the study is assessment of the resin curing process temperature using a pyrometer. It can be stated that the pyrometer measurement gives similar results to the thermocouple measurement (it was previously observed in [1] and [4]). It shows slightly lower temperatures practically in the entire measurement range, due to the more intense heat transfer to the outer environment, but it is a constant value for a given temperature profile. The data from the thermocouple and the pyrometer used together can be a valuable tool to validate the thermodynamic models of systems similar to those analyzed in the study.

CONCLUSIONS

Based on the obtained results and the performed observations, the following conclusions were drawn:

1. Filling the resin with fragmented glass fabric caused a decrease in the peak temperature of the curing process and extended the time of reaching this temperature. These effects were found to intensify with increasing the weight of the filler. It can be claimed that the filler has inhibitory effect on the curing reaction.
2. Filling the resin with fragmented glass fabric slightly increases the gelation time.

3. The observed effects indicate an increase in the thermal insulation of the curing mass, along with an increase in the content of glass fiber filler.
4. The obtained results indicate that the presence of the fibers leads to stabilization (better repeatability) of the resin curing process.
5. The pyrometer measurement can effectively be used to analyze resin curing progress as a complement or substitute for precise thermocouple measurements.

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