

The effect of the heat treatment on the crosslinking of epoxy resin for aviation applications

Mateusz Mucha^{1),*}, Tomasz Sterzyński²⁾, Aneta Krzyżak¹⁾

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Abstract: We have investigated the MGS L285 epoxy laminating resin system, used in aviation applications. A number of tests were carried out, namely Dynamic Mechanical Analysis (DMA), Differential Scanning Calorimetry (DSC), tensile testing, three-point bending flexural testing, Charpy impact testing, Shore D hardness, density measurements and Fourier-Transform Infrared spectroscopy (FT-IR). Moreover, the tensile toughness U_{TT} , the brittleness B and the linear isobaric thermal expansivity α_L were calculated. The samples were subjected to heat treatment in the temperatures of 50, 60 and 80°C for 15 hours or were stored in room temperature. Glass transition temperature, hardness, density as well as other properties were observed to rise along with the increasing heat treatment temperature, suggesting the validity of applications of Voronoi-Delaunay structural analysis to polymer science. On the other hand, properties such as brittleness, toughness and impact strength exhibited a non-linear course of changes as a function of the heating temperature.

Keywords: epoxy resin, heat treatment, crosslinking, aviation.

Wpływ wygrzewania na sieciowanie żywicy epoksydowej przeznaczonej do zastosowań w lotnictwie

Streszczenie: Badano laminującą żywicę epoksydową MGS L285 przeznaczoną do zastosowań w lotnictwie. Przeprowadzono dynamiczną analizę mechaniczną (DMA), skaningową kalorymetrię różnicową (DSC), statyczną próbę rozciągania, zginanie trójpunktowe, badanie młotem Charpy'ego, pomiary twardości metodą Shore'a D, pomiary gęstości, zarejestrowano także widma metodą skaningowej spektroskopii transformatorowej Fouriera (FT-IR). Obliczono wartości wiązkości U_{TT} , kruchości B i izobarycznej rozszerzalności termicznej α_L . Próbkę wygrzewano w temperaturze 50, 60 lub 80 stopni Celsjusza przez 15 h lub przechowywano w temperaturze pokojowej. W odniesieniu do dużej części badanych właściwości zaobserwowano ich poprawę wraz z rosnącą temperaturą wygrzewania. Korelacja temperatury zeszklenia, twardości i gęstości polimerów wskazuje na słuszność zastosowania w badaniu wolnych objętości analizy strukturalnej opartej na triangulacji Delone i diagramach Woronoja. W wypadku właściwości, takich jak: kruchość, wiązkość i udarność stwierdzono nieliniowy przebieg zmian w funkcji temperatury wygrzewania.

Słowa kluczowe: żywica epoksydowa, wygrzewanie, sieciowanie, lotnictwo.

Currently, the composites based on epoxy resin are regarded as most important material used in aviation, for structural elements [1–9], including aircraft skin [10, 11]. In order to meet increasing expectations, more and more research is being conducted to modify the properties of the resin by adding fillers [12–16], including the increasingly popular nanofillers [17–25]. An important challenge for all technical applications of epoxy resin based com-

posites, particularly aviation constructions, is the need to manufacture materials with significantly reduced flammability [26–29]. However, fillers can reduce the gel time of the resin [30, 31], and therefore alter the manufacturing process. For example, it was found that water contained in fillers may cause an acceleration of the resin/hardener reaction [32]. On the other hand, for some epoxy resins, the heat treatment is necessary to achieve the properties required in aviation [33, 34].

In order to properly assess the effect of the filler on the resin, it is necessary to know thoroughly the crosslinking process of the neat resin [35–42]. In particular, it is advisable to determine the effect of heat treatment on the resin properties [43–46]. For example, in case of the concrete based on epoxy resin mixed with isophorone diamine (IPDA) hardener, higher curing temperature (in a range to

¹⁾ Military University of Aviation, Faculty of Aviation, Dywizjonu 303 35, 08-521 Dęblin, Poland.

²⁾ Poznan University of Technology, Polymer Division, Institute of Materials Technology, Piotrowo 3, 61-138 Poznań, Poland.

^{*} Author for correspondence: m.mucha@law.mil.pl

60°C) resulted in an improved modulus of elasticity and ultimate compressive, as well as flexural strength [47].

One of usually applied technique to study the crosslinking of the resin is to determine its hardness. The Dynamic Mechanical Analysis (DMA) and Differential Scanning Calorimetry (DSC) allow to define the thermal properties of the resin, in particular the region of the glass transition T_g [48–52]. The typical Fourier Transformed Infra-Red spectra for epoxy resin are known, so any additional peaks obtained during FT-IR-measurements will inform about the unusual behavior of the material [53, 54].

The subject of the study is the MGS L285 laminating resin system, that is commercially available and commonly used in aviation [55]. According to the technical specification provided by the manufacturer, after a heat treatment at 50–55°C, the system meets the standards for gliders and motor gliders, and after a heat treatment at 80°C, it satisfies the standards for motor planes [32]. The purpose of this work is to obtain a better understanding of the process of crosslinking of the resin, and particularly the influence of post-heat treatment on the cured epoxy resin.

EXPERIMENTAL PART

Materials

The objective of the studies was EPIKOTE resin MGS LR 285 and EPIKURE curing agent MGS LH 285. Laminating resin L285 is a mixture of epoxy resin (number average molecular weight ≤ 700), which is a reaction product of bisphenol-A (epichlorhydrin) (50–75 wt %) and 1,2,3-propanetriol, glycidyl ethers (50–75 wt %). H285 hardener is a mixture of 3-aminomethyl-3,5,5-trimethylcyclohexylamine (75–90 wt %), phenol, 4,4'-(1-methylethylidene)bis-, polymer with 5-amino-1,3,3-trimethylcyclohexanemethanamine and (chloromethyl)oxirane (5–13 wt %), benzyl alcohol (5–10 wt %), 4-nonylphenol, branched (0–1.1 wt %), 3-aminopropyltriethoxysilane (0–1 wt %). The information of basic physical and chemical properties of the resin and the hardener are presented in Table 1 [32].

Sample preparation

After mixing the resin with the amine curing agent, samples were cast into PTFE molds for 24 hours. Then, one out of four groups of samples was stored at room temperature of 23°C, and the other three groups were subjected to heat treatment at 50, 60 and 80°C, respectively. The temperature range of up to 80°C was based

on the manufacturer's recommendations, although it can be estimated that higher temperature value would result in a higher degree of conversion of functional groups of the polymer [56].

The majority of samples were prepared with 100 : 40 mass ratio recommended by the manufacturer. However, in order to have more insight in the curing process, specimens for hardness and density testing were also prepared with 100 : 30 and 100 : 50 ratios.

Methods of testing

Dynamic mechanical analysis

The DMA allowed determining the complex modulus, in a range of temperatures from ambient conditions to 150°C. Plots of storage and loss modulus obtained with the heating rate of 2.0°C/min, were used to locate the glass transition temperature region and $T_{g,DMA}$, as well as determining storage modulus E' at room temperature (25°C).

DMA testing was performed using the Anton Paar MCR301 rotational rheometer. Specimens of a rectangular form [50.0 × 10.0 × 3.0 (mm³) nominal dimensions] were analyzed by torsion, one per each of the four heat treatment temperatures. The sinusoidal stress at frequency $f = 1.0$ Hz (typical value for DMA [57]) as a function of time was imposed, reaching a peak value for normal force of 1.0 N, applied in the grip at a distance from the axis of rotation. This resulted in a cyclic deformation of the sample. The number of data points was 281 per sample.

Differential scanning calorimetry

The DSC was used to determine the glass transition temperature $T_{g,DSC}$ [49, 57–64]. One sample per each heat treatment temperature was tested on Differential Scanning Calorimeter Netzsch Phoenix 204 F1 apparatus, in accordance with ISO 11357 standard [65]. The heating and cooling rate were set at 10.0°C/min and the temperature range between -60 and 200°C.

Tensile testing

The tensile testing was carried out to obtain the values of tensile strength, Young's modulus E_r , the ultimate tensile strength σ_m , the tensile strain at tensile strength ε_m , the fracture strength σ_b , and the strain at break ε_b based on the stress-strain (σ - ε) curves. Moreover, the area underneath the stress-strain curve was calculated

Table 1. Properties of MGS L285 epoxy resin and H285 hardener measured at 25°C [32]

	Density g/cm ³	Viscosity mPa·s	Epoxy equivalent g/equivalent	Epoxy value equivalent/100 g	Amine value mgKOH/g	Refractory index
Laminating resin L285	1.18–1.23	60–900	155–170	0.59–0.65	–	1.525–1.530
Hardener H285	0.94–0.97	50–100	–	–	480–550	1.502–1.550

to obtain the tensile toughness U_{TT} . The values of E' and ε_b were used to calculate the brittleness B , to evaluate the linear isobaric thermal expansivity α_L .

The tensile properties of 40 bone-type (1BA) samples (10 per each heat treatment temperature) were determined in accordance with ISO 527 standard on Zwick/Roell Z5.0 machine, with the test speed of 1 mm/min.

The toughness U_{TT} was calculated in accordance with Eq. (1) defined in [66]:

$$U_{TT} = \int_0^{\varepsilon_b} \sigma \delta \varepsilon \quad (1)$$

The brittleness B was determined in accordance with Eq. (2) defined in [67]:

$$B = 1/(E' \cdot \varepsilon_b) \quad (2)$$

The isobaric thermal expansivity α_L was calculated in accordance with Eq. (3) defined in [68]:

$$\alpha_L = 104 \cdot B^{0.132} \quad (3)$$

Flexural testing

The three-point bending flexural testing provided values of the modulus of elasticity in bending E_f , the maximum flexural stress σ_{fM} and the failure strain ε_{fM} . The flexural properties of 40 rectangular form [80.0 × 10.0 × 4.0 (mm³) nominal dimensions] samples (10 per each heat treatment temperature) were determined in accordance with ISO 178 standard, by means of the Zwick/Roell Z5.0 universal testing machine, operating by test speed of 2 mm/min.

Impact testing

The amount of energy absorbed by material at fracture, was determined by means of the Charpy impact testing. The measurements of Charpy impact properties of 40 rectangular form [80.0 × 10.0 × 4.0 (mm³) nominal dimensions] samples (10 per each heat treatment temperature) were per-

formed on Galdabini – Impact 25 tester, in accordance with ISO 179-1 standard. The Charpy striker, with 7.5 J energy and 1fU method were set for the testing.

Values of B and U_C were compared with Eq. (4) defined in [69]:

$$U_C = a_c + 1/\tan h(b_c \cdot B) \quad (4)$$

where parameters $a_c = -0.640$, and $b_c = 1.63$ were calculated by Brostow *et al.* in [69].

Hardness testing

In order to determine Shore D hardness, in accordance with ISO 868 standard, the set of 10 samples was tested per each heat treatment temperature, as well as each resin/hardener mass ratio.

Density measurements

The density measurements were performed for one sample per each heat treatment temperature, as well as each resin/hardener mass ratio, on a precision laboratory scale Mettler Toledo XSE205, with an accuracy of 0.01 mg. Also the immersed solid body method was applied. As a liquid, distilled water at a room temperature was used.

FT-IR

One sample per each of the four heat treatment temperatures was examined on Jasco FT/IR-4600 Fourier transform infrared spectrometer with 40 measurements per one spectrum, at the measurement range between 4000 cm⁻¹ and 400 cm⁻¹.

RESULTS AND DISCUSSION

Thermal properties

Storage (E') and loss (E'') module obtained in DMA tests were plotted in Fig. 1. The glass transition tempera-

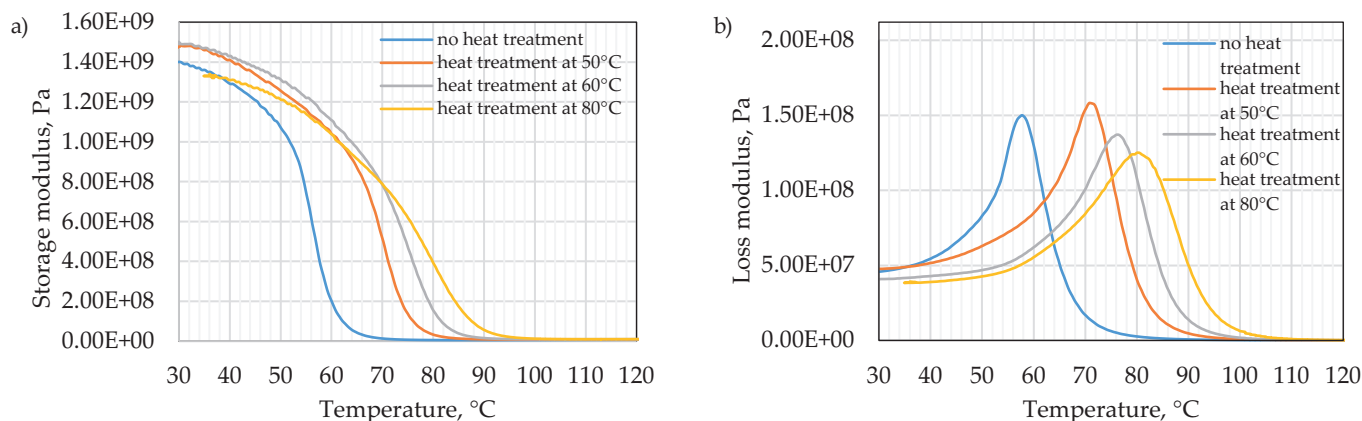


Fig. 1. Effect of the heat treatment at room temperature: 50, 60 and 80°C on the DMA run: a) storage modulus E' , b) loss modulus E''

Table 2. Glass transition temperature ranges obtained in DMA and DSC measurements of epoxy resin heated in four different temperatures

Heat treatment	Glass transition temperature range, °C	$T_{g\text{DMA}}$, °C	$T_{g\text{DSC}}$, °C
No heat treatment	38.7–74.0	57.8	67.9
Heat treatment at 50°C	44.4–87.4	71.0	72.8
Heat treatment at 60°C	51.7–93.3	76.3	75.3
Heat treatment at 80°C	51.9–99.9	80.3	85.4

ture ranges, as well as $T_{g\text{DMA}}$, are presented in Table 2, while storage modulus E' in ambient conditions is presented in Table 3. It is noticeably that for higher heat treatment temperature a shift of the storage modulus and loss modulus plots, versus higher temperature was noted, denoting a certain improvement of thermal stability, due to enhanced crosslinking of the resin. However, as far as E' in ambient conditions is concerned, its values for 50 and 60°C heat treatment temperature are higher than for 80°C and for no heat treatment samples.

The values of $T_{g\text{DSC}}$ are presented in Table 2. Although the midpoints of glass transition regions obtained in DSC are slightly higher than values of $T_{g\text{DMA}}$, they confirm a similar trend, that is a relationship between the glass transition temperature ranges and the heat treatment temperature. It is known that the values of $T_{g\text{DMA}}$ are strongly dependent on measurement frequency. Thus higher values of $T_{g\text{DSC}}$ compared to $T_{g\text{DMA}}$ may be correlated to the DMA measurements condition, when the samples are submitted to sinusoidal changing deformation. It is not the case of DSC investigations, which may be treated as practically static [49, 57–59].

Mechanical properties

The tensile testing and the three-point bending testing results are presented in Table 4, where a relation between

the heat treatment temperature and mechanical properties is visible.

The rise in heat treatment temperature leads to an increase of tensile strength σ_m , maximal flexural stress σ_{fm} , and of deformation ϵ_m and ϵ_{fm} . A lower impact on elastic modulus in tensile E_t and bending E_f was noted moreover. The highest increase for the majority of mechanical properties was observed for the samples heated at 50°C, compared to the non-heated samples. On the contrary, the value of elongation at break ϵ_b remains practically constant, with a slight increase for samples treated at 60°C.

The toughness U_{TT} exposes the highest value by the sample heated at 60°C.

A significant difference in U_{TT} was found between the non-heated and thermally treated samples. The values for heated samples are higher than the result presented in [71] for pre-cured at 50°C for 4 h and post-cured at 70°C for 6 h epoxy resin.

The brittleness B values indicate that materials without heat treatment and those heated in 80°C are generally more brittle comparing with heat treated at 50 and 60°C (Table 3). All brittleness values, likewise the thermal expansivity evaluated on the basis of Eq. (3), are most similar to styrene/acrylonitrile copolymer (SAN), among materials described in [69]. Although it is known that “brittleness is not an inverse of toughness” [72], a close

Table 3. Storage modulus at ambient conditions E' obtained in DMA, brittleness B , linear isobaric thermal expansivity α_L and impact strength U_C of epoxy resin heated in four different temperatures

Heat treatment	E' , Pa	B , % · Pa/10 ¹⁰	α_L , 10 ⁻⁶ /K	U_C , J/cm ²
No heat treatment	1.35E+09	1.38	108.5	1.84
Heat treatment at 50°C	1.45E+09	1.21	106.7	2.04
Heat treatment at 60°C	1.46E+09	1.12	105.6	1.93
Heat treatment at 80°C	1.34E+09	1.30	107.7	1.98

Table 4. Mechanical properties of epoxy resin, by tensile and bending testing, heated in four different temperatures

Heat treatment	Tensile testing						Three-point bending		
	E_t , GPa	σ_m , MPa	ϵ_m , %	σ_b , MPa	ϵ_b , %	U_{TT} , J/m ³ · 10 ⁴	E_f , GPa	σ_{fm} , MPa	ϵ_{fm} , %
No heat treatment	2.3	52.7	3.7	25.4	6.1	213.7	3.0	100.6	4.3
Heat treatment at 50°C	2.6	73.8	4.9	66.0	6.0	307.8	3.1	118.5	5.5
Heat treatment at 60°C	2.4	74.2	5.3	66.3	6.7	358.5	3.1	124.4	5.8
Heat treatment at 80°C	2.4	76.2	5.4	73.3	6.2	326.7	3.3	133.4	5.9

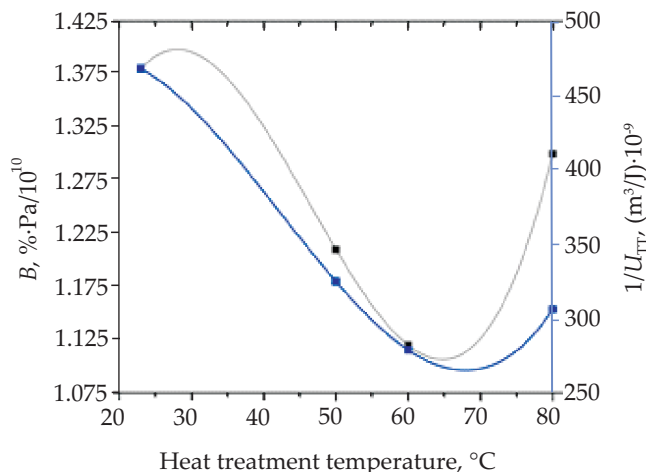


Fig. 2. The correlation between the brittleness B , the inverse of tensile toughness U_{TT} and the heat treatment conditions

correlation between the third degree polynomial fits of B and $1/U_{TT}$ as functions of heat treatment temperature can be observed at Fig. 2.

Moreover, the Table 3 contains the values of α_L calculated on the basis of brittleness. The obtained results indicate that the values provided for the epoxy resin in [70] are twice too low.

The values of Charpy impact strength U_C for samples treated in different temperatures are presented in Table 3. The values obtained for no-thermally treated samples are in accordance with [73]. A moderate effect of the heat treatment on U_C was noted. The dependence of U_C on B is presented in Fig. 3. The evaluated points form the same line as U_C plot (representing the equation given by Brostow *et al.* in [69]), although transferred to higher values of impact strength. As it follows from Fig. 3, in a quasi linear domain of an impact/brittleness relationship, the comparable U_C values of approximately 2 J/cm^2 correspond with B values at the range between 1.1 and $1.4 \text{ \%} \cdot \text{Pa}/10^{10}$.

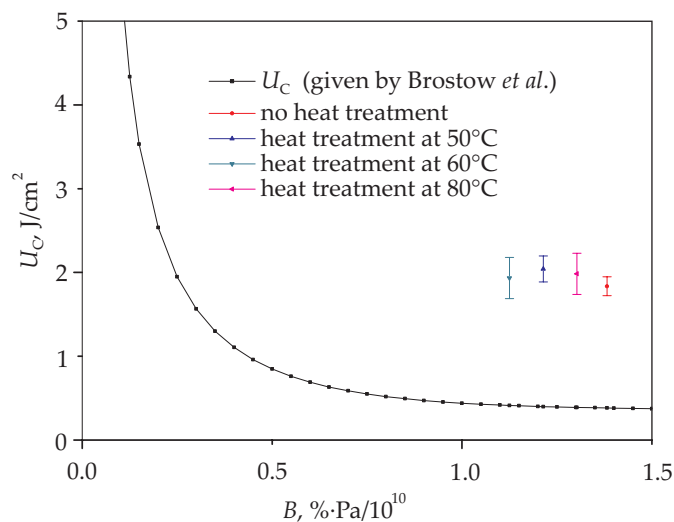


Fig. 3. The Charpy impact strength U_C as a function of brittleness B for samples treated at various temperatures

The effect of heat treatment on the Shore D hardness is presented in Fig. 4 with corresponding standard errors. The results for resin/hardener mass ratios of 100 : 30, 100 : 40 and 100 : 50 are depicted on this figure. As it follows from the graph, a significant difference of hardness between non-heated and heated samples was noted, where an increase from Shore D = 55 to approximately 73–83 is probably be due to the substantial role of thermally stimulated cross linking of the epoxy resin, with the lowest hardener content. For the 100 : 40 samples, this increase between about 76 and 83 Shore D values is much less evident, although it indicates an essential role of heat treatment by hardening this type of resin. Any improvement of hardness was noted for the ratio 100 : 50, *i.e.* the hardener content which exceeded the producer's recommendations.

Density

The effect of heat treatment on the density of samples with resin/hardener mass ratios of 100 : 30, 100 : 40 and 100 : 50 is presented in Fig. 5. The highest ρ values of approximately 1.181 g/m^3 to 1.186 g/m^3 were noted for the samples with the lowest hardener content, and the lowest density values, in the range between 1.154 g/m^3 and 1.158 g/m^3 for epoxy resins solidified by the highest hardener content. This effect may be due to various density of resin and hardener (see Table 1). As the applied hardener has a lower density, consequently the 100 : 30 samples reveal a higher density than the samples 100 : 40 and 100 : 50.

A slight rise in the density with the heat treatment was also noticed. The difference between the value of the unheated 100 : 40 sample and the one heated at 80°C , referred to the density of the unheated sample, equals approximately 0.5%. Although this change is almost invis-

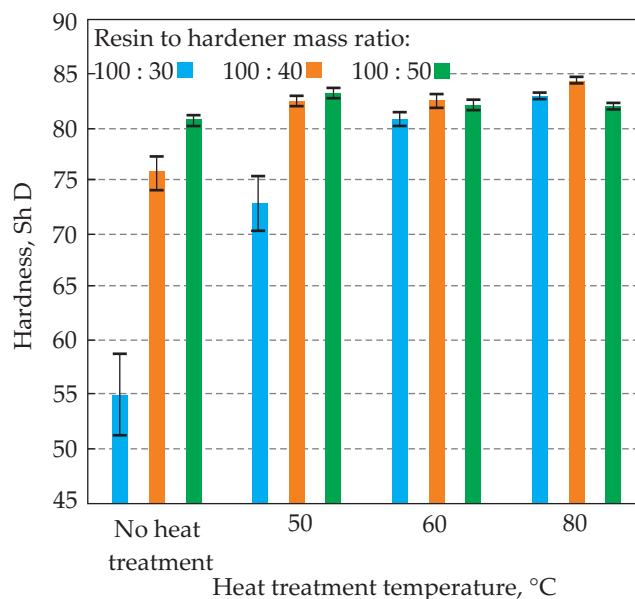


Fig. 4. Effect of thermal treatment and resin/hardener mass ratio on the Shore D hardness mean values

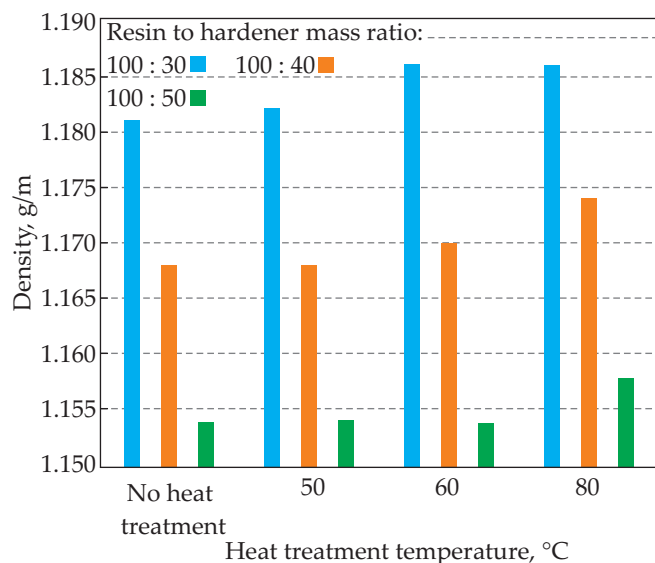


Fig. 5. The effect of thermal treatment and resin/hardener mass ratio on the density

ible in comparison to the one resulting from different mass ratios, it occurs for all resin/hardener concentrations.

FT-IR

The FT-IR spectra are presented in Fig. 6. As it may be seen, each of the four lines on the chart reveals the same course of peaks, characteristic for epoxy resin, namely at 3365, 2925, 2855, 2314, 1607, 1507, 1457, 1241, 1181, 1035, 828 and 559 cm^{-1} . As no additional peaks was detected, a conclusion may be formulated that beside crosslinking no other changes in the chemical structure of the polymer network, during curing of the resin, are sufficiently significant to be observed on the FT-IR spectra.

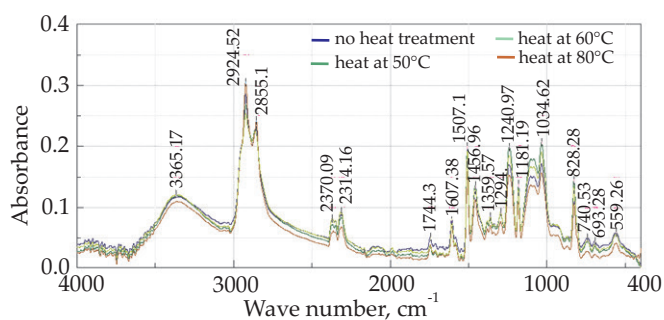


Fig. 6. The FT-IR spectra at a measurement range between 4000 cm^{-1} and 400 cm^{-1} for the epoxy samples with various heat treatment

CONCLUSIONS

A shift of the glass transition temperature regions versus higher values was due to thermal treatment induced improvement of the crosslinking, as found by DMA and DSC measurements. This effect, also apparent at higher density, hardness measurements, as well as tensile and flexural strength may support the idea of a correlation

between chain topology, free volume, and the glass transition temperature T_g , as suggested by Kalogeras *et al.* in [74]. Free volume distribution can be determined according to the Voronoi-Delaunay approach, which combines molecular dynamics and Voronoi tessellation analysis. In order to achieve this goal, Delaunay simplices and Voronoi polyhedra are constructed for the set of points determined by the chain topology. For example, the application of Voronoi-Delaunay structural analysis, extracted for a linear chain polymer, led to the conclusion that the average volume of the Voronoi polyhedron around the particles of the polymer decreases with increasing length of the chain, resulting in a reduction of free volume [75].

By certain properties, such as elongation at break ϵ_b , toughness U_{TT} , impact strength U_C , storage modulus E' as well as inverse of brittleness $1/B$ and inverse of linear isobaric thermal expansivity $1/\alpha_L$ higher values were observed for samples treated at 50°C or/and 60°C, indicating a non-linear temperature dependence of properties at these thermal conditions. Moreover it may be suggested that the tendency to increase at this region (as in the case of σ_m) is balanced by an increasing tendency to crack.

In the case of an investigated material, it is not a general rule that the effect of heat treatment on brittleness B is almost the same as on an inverse of toughness $1/U_{TT}$.

The examination of various resin/hardener ratios allowed on tracing the effect of heat treatment on the curing process. A lower mass fraction of the hardener than in 100:40 ratio (namely 100:30 ratio) results in lower crosslinking of the resin, although the resulting differences in hardness values may be equalized by the heat treatment of 60°C or higher.

On the contrary, no significant indication of the chemical modification due to the heat treatment of the epoxy resin, was found by the FT-IR analysis of the post heated samples.

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