ENHANCEMENT OF THERMAL AND ELECTRICAL CONDUCTIVITY OF CFRP BY APPLICATION OF CARBON NANOTUBES

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Abstract
The aim of the work was to improve the thermal and electrical conductivities of CFRP by enhancement of epoxy matrix thermal and electrical properties. To achieve the goal multi-wall carbon nanotubes (CNTs) were applied as a filler. CNTs were dispersed in epoxy resin using three roll milling. Nanocomposites with weight amount varied from 0.05 to 1% were fabricated and studied. Scanning and transmission electron microscopies were used for CNTs dispersion control. Thermal diffusivity and electrical conductivity were also measured. Rheological parameters, such as viscosity, storage and loss modulus were tested. CNTs significantly increase the viscosity of neat epoxy, what makes difficult the infiltration of carbon fibres. An addition of solvent was applied for decreasing the viscosity of epoxy with CNTs. Influence of the solvent on thermal and electrical conductivity, as well as mechanical properties was investigated. Application of CNTs increases the thermal and electrical conductivity, mechanical properties, however decreases the curing time and viscosity.

1. Introduction

Epoxy resins are characterized by high mechanical properties, dimensional stability and chemical resistance. Due to such properties they have found their applications in many fields, e.g. aircraft, aeronautics, electronics, coatings. The main disadvantage of epoxy resin used especially in aircraft application is too low thermal and electrical conductivity. The disadvantages reduce application of epoxy resin in new fields [1].
Carbon nanotubes are characterized with high mechanical properties, high aspect ratio and large surface area. They exhibit high thermal and electrical conductivities. Moreover, they are resistant to high temperatures both in air and nitrogen atmosphere. Even a small addition of CNTs can increase conductivity by a few orders of magnitude. Idea of application of CNTs in polymer matrix seems to be very promising [2, 3]. It is widely expected that CNTs can improve the mechanical and thermal properties. However, CNTs are also characterized by strong tendency to agglomerate. It is difficult to obtain uniform dispersion in polymer matrix. Different methods are applied, such as mechanical stirring, ultrasonication, calendaring, or combination of these methods [4, 5]. Some of these methods lead to the improvement of CNTs dispersion but also can cause the CNTs damage. Too high shear forces can destroy CNTs what influences on the composite properties. As the result the conductivity is also

lower. Sometimes modifications of CNTs surface are applied. However, modification incorporates sp^3 hybridization defects. Following the reduction of conductivity is observed [4]. It is reported in the literature that composites with non-modified CNTs exhibit higher electrical conductivity [3].

Recently an increase of carbon fiber reinforced polymers CFRP application in many fileds of industry is observed, especially in transport [6]. Also an increase of publications concerning CFRP composites with CNTs can be noticed [7]. Introduction of CNTs in CFRP can lead to the improvement of mechanical properties, can play the role of shielding against electromagnetic waves, improve thermal stability and help in heat distribution. CNTs can also be used for structure health monitoring or for deicing systems [8]. Application of CNTs to CFRP seems to be very promising concept for improvement of thermal and electrical conductivities not only in plane but also through the material thickness.

The aim of this work was to improve thermal and electrical conductivity of CFRP by addition of CNTs. In this work epoxy resin was used as polymer matrix. CNTs were mixed with epoxy resin using three roll milling. Light microscopy was used for preliminary evaluation of calendaring parameters. In the first step epoxy matrix with CNTs was characterized. Scanning electron microscopy observations were done for evaluation of CNTs dispersion. Bending strength, thermal and electrical conductivities were also measured. Rheological characteristic was performed. As the result, the CNTs weight fraction, which gives the highest thermal and electrical conductivity, was found. Therefore, 1 wt.% of CNTs was selected for CFRP fabrication using hand lay-up method. It is well known that addition of CNTs significantly increases the viscosity of the matrix. In order to decrease the mixture viscosity for better carbon fabrics impregnation styrene solvent was applied. Effect of styrene addition on thermal, electrical and mechanical properties of epoxy/CNTs nanocomposites and CFRP were investigated.

2. Experimental

2.1. Materials

In this research neat epoxy Biresin CR 174 and curing agent CH 174 (100:40) supplied by Sika were used. Neat epoxy resin is characterized with viscosity of 700- 1000 mPas in 25°C, 240 minutes of life time in 18- 23°C and glass transition temperature equal to 174°C. CNTs NC7000 supplied by Nanocyl with 90% of purity, 1.5 µm average length, 9.5 nm average diameter and surface area equal to 250- 300 m^2/g were applied. 2D carbon fabrics GG 160 P with the plain wave and areal weight of 160 g/m^2, supplied by Havel Composites were used for laminates manufacturing.

CNTs were dispersed in epoxy resin by three roll milling. First, CNTs were mechanically mixed with epoxy resin. Then, the mixture was applied between rolls and mixed several times reducing the gap between rolls from 50 to 10 µm. Mixtures with CNTs amount below 1wt.% were prepared by dilution of 1wt.% concentrate and mixing between rolls. Such prepared resin with assumed weight fraction of CNTs was mechanically stirred with curing agent and cured by 12 hours at 70°C.

Laminate was fabricated using hand lay-up method from 2D carbon fabrics and neat epoxy resin filled with CNTs. As the reference sample also laminate without CNTs was prepared. In each case 4 layers of fabrics [0/90°] were applied. The laminate was cured at 25°C by 24h and subsequently at 70°C by 12h.

2.2. Measurements

Light microscope BIOPLAR PI was used for preliminary selection of calendaring parameters. CNTs dispersion was controlled with high resolution SEM Hitachi S5500. Bending strength was measured by three point bending test on MTS Q/Test 10 machine, according to PN-EN ISO 178:2011/A1:2013-06E standard. Thermal diffusivity was measured with LFA 447 NanoFlash for 4 temperatures: 25, 60, 100, and 140 ^{O}C, respectively. Rheological tests were carried out using rheometer ARES TA Instruments with 25 mm in diameter plate-plate set-up and gap between plates equal to 0.5 mm. Viscosity, as well as storage and loss modulus were measured. Dynamic time sweep mode was applied, with constant value of deformation equal to 10 % and frequency of 1 Hz. Electrical conductivity was measured using Keithly model 2182A/622x. Measured values of voltage and electrical current were used for calculation of conductivity.

3. Results and discussion

Light microscopy was used for selection of dispersion parameters (fig. 1). After each time of calendaring the dispersion was controlled taking a small probe of the mixture. After second time the gap between rolls was reduced to decrease the agglomerates size visible in the microstructure. Because still CNTs agglomerates were visible as black spots the gap was reduced to 10 μm. The calendaring was finished when the mixture achieved uniform colour. Then the nanocomposites were cured and high resolution scanning and transmission electron microscopy observations of CNTs distribution were done.
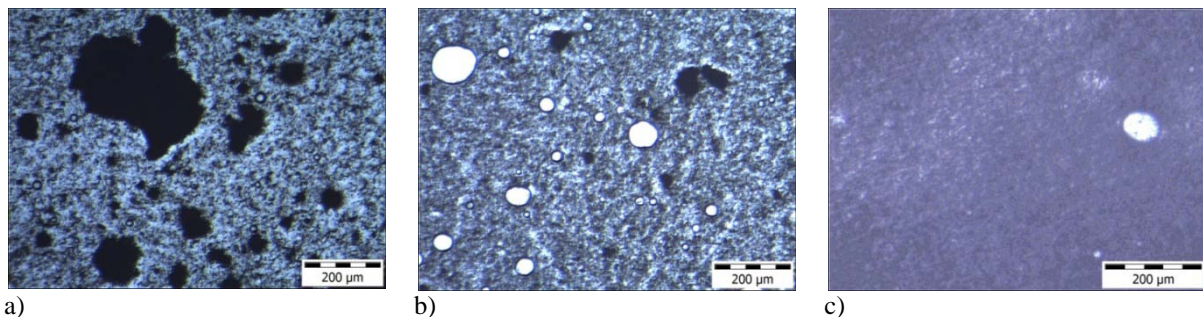

a) b) c)

Figure 1. Microstructure of epoxy resin with CNTs mixture after calendaring by: a) 1-time, b) 2- times, c) 6-times.

In fig. 2. the microstructure of brittle fracture of epoxy nanocomposite with 1 wt.% of CNTs is shown. HRSTEM images show uniform dispersion of CNTs in epoxy matrix. None agglomerates were found.
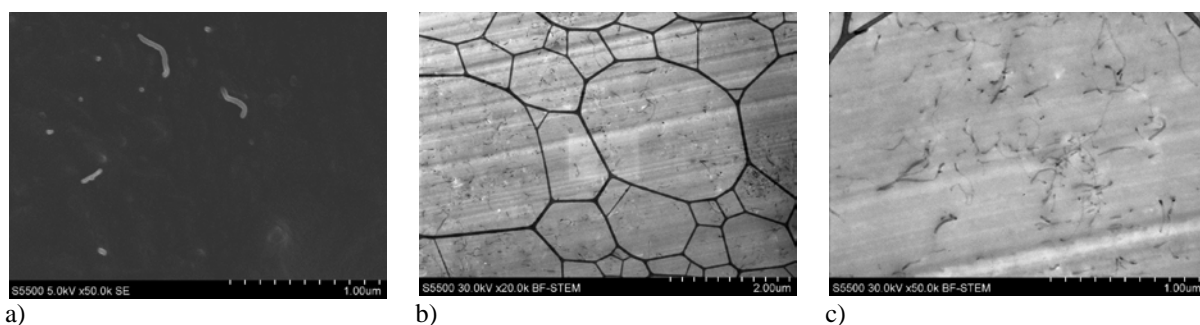

a) b) c)

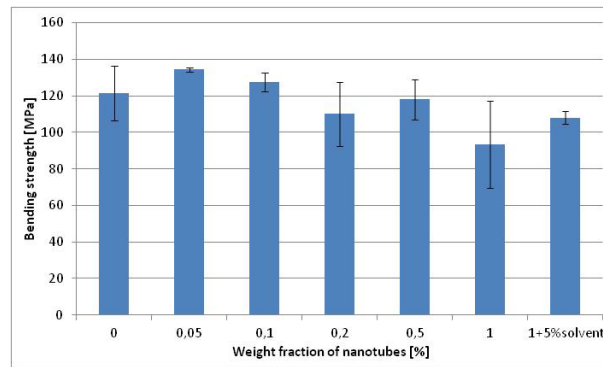**Figure 2.** Images of epoxy/CNTs nanocomposite with 1 wt.% of CNTs: a) SEM, b), c) TEM.

Figure 3. Bending strength of nanocomposites vs. CNTs weight fraction.

It is well known that small addition of CNTs can enhance the mechanical strength of epoxy resin. However, due to the increase of viscosity with the increase of CNTs content the samples with discontinuities and defects like voids or bubbles are obtained [9]. Such high viscosity hinders casting of resin with CNTs without using high pressure. Therefore, for the higher CNTs content the decrease of bending strength was observed, as shown in fig. 3. Moreover, the non repeatable values of bending strength are shown as standard deviation (SD) bars. It can be noticed that the highest SD was recorded for 1 wt% of CNTs. In order to reduce the viscosity of resin with 1 wt% of CNTs the solvent was applied. The addition of 5 wt.% of styrene leads to the fabrication of samples with higher bending strength and lower SD, what means that due to decreasing of the viscosity samples without defects were obtained.
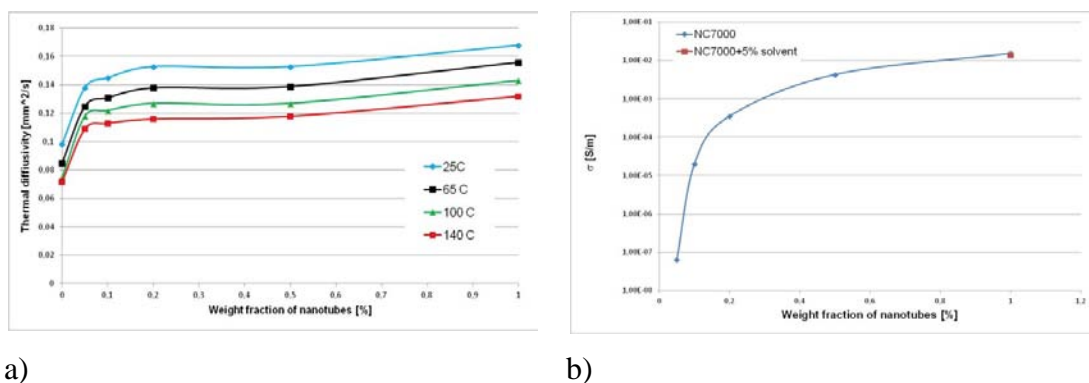

a)   b)

Figure 4. a) Thermal diffusivity, b) electrical conductivity of nanocomposites with different CNTs content.

The results of thermal diffusivity as a function of CNTs weight fraction, measured at four temperatures are shown in fig. 4a. Independently on the measurement temperature the thermal diffusivity increases with the increase of CNTs amount. Sudden growth in thermal diffusivity is observed up to 0.2 wt.% of CNTs, then the thermal diffusivity stabilizes, slightly increasing for 1 wt.% of CNTs. It was reported in the paper [10], that addition of 1 wt.% of single-wall CNTs increased the thermal conductivity of epoxy resin twice in the contrary to the same weight fraction of carbon fibers, which increased the thermal conductivity of approx. 40%.

With the increase of CNTs weight fraction an increase of electrical conductivity was also obtained, as shown in fig. 4b. Addition of 1 wt% of CNTs increases conductivity in a few orders of magnitude. For sample fabricated with the application of styrene any meaningful changes of conductivity were observed in comparison to the sample without solvent addition. It is known that well dispersed CNTs can improve significantly electrical conductivity [11, 12]. It is also reported that in the case of laminates CNTs increase the electrical conductivity

through the thickness by one order of magnitude while in the other two directions the conductivity is not considerably affected [13].

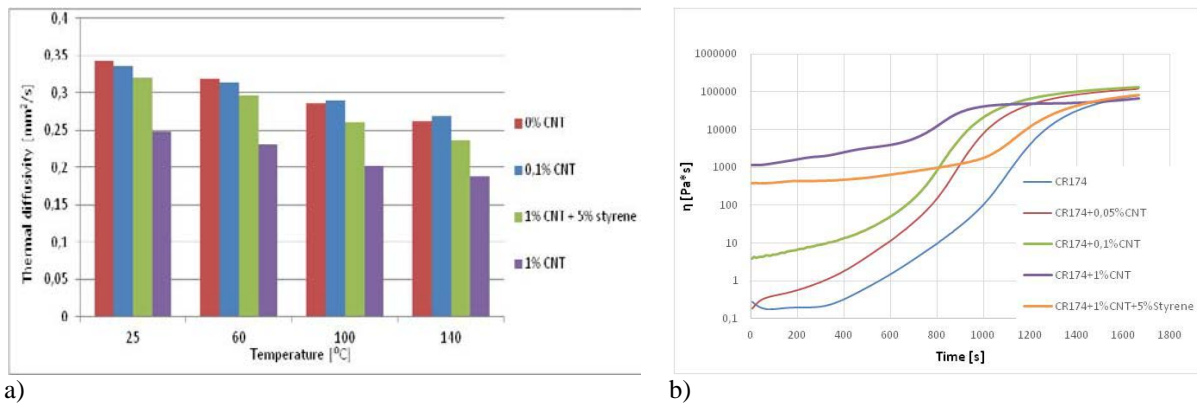In our studies thermal diffusivity was measured through the laminate thickness.

a)   b)

Figure 5. a) thermal diffusivity of laminates without and with CNTs and styrene as well, b) viscosity of epoxy resin system (neat epoxy + curing agent) with different CNTs weight fraction..

In fig. 5a the results of thermal diffusivity of CFRP laminates with CNTs weight fractions varied from 0.1 to 1 wt.% are shown in comparison to the laminate without CNTs. No significant changes in thermal diffusivity were observed after introduction of 0.1 wt.% of CNTs to the epoxy matrix. Further increase of CNTs content leads to the decrease of laminate thermal diffusivity. Addition of CNTs significantly increases the viscosity. The changes in viscosity of epoxy system consisting of Biresin CR 174 and curing agent CH 174 with the addition of different weight fraction of CNTs and solvent are shown in fig. 5b. For sample with 0.1 wt.% of CNTs an increase of viscosity by one order of magnitude is observed. Addition of 1 wt.% leads to the viscosity increase of about three orders of magnitude. CNTs effect on the viscosity because of their extremely high surface area and aspect ratio. The same tendency was reported in the papers [9, 14, 15]. Because of too high viscosity during fabrication of CFRP the styrene was added to decrease the viscosity of resin system. In the case of 5 wt.% addition of styrene to the mixture with 1 wt.% of CNTs the decrease of viscosity is almost in one order of magnitude. Such reduction of viscosity is meaningful from the technological point of view. Due to the significant increase of the viscosity with the increase of CNTs weight fraction the poor impregnation of carbon fabrics was obtained. Also defects like voids or bubbles, as well as other structural discontinuities are observed, as shown in fig. 6.
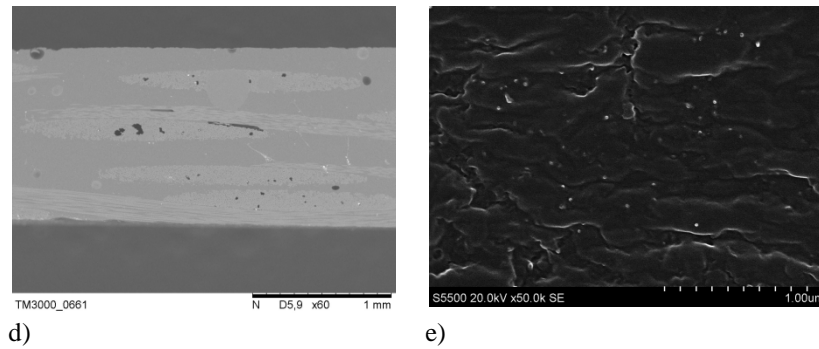

a)   b)   c)
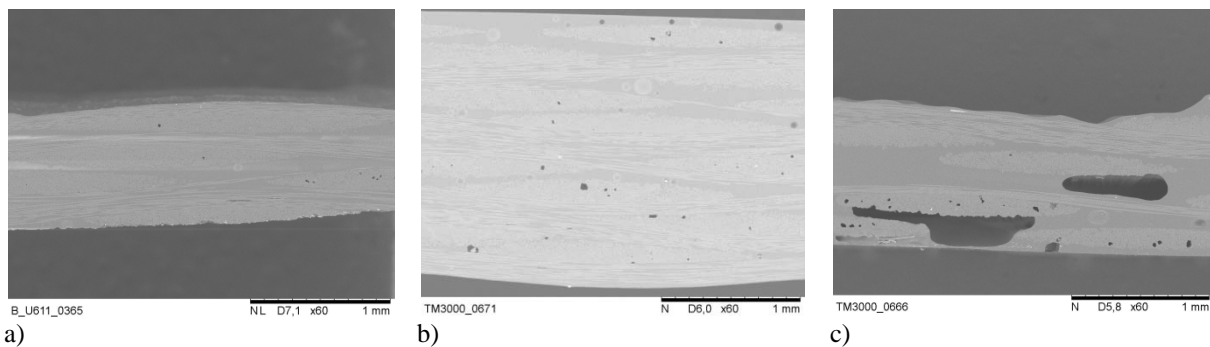
Figure 6. SEM images of CFRP cross section with CNTs: a) 0 wt.%, b) 0.1 wt.%, c) 1 wt.%, d), e) 1 wt.% and 5 wt.% of styrene.

The size of pores increases with the increase of epoxy resin system viscosity due to the increase of CNTs weight fraction. The structural discontinuities are the reason of thermal diffusivity drop for 1 wt.% of CNTs. Application of styrene leads to the better fibres impregnation due to the lower viscosity (fig. 6d). Less amount of defects leads to the significant increase of thermal diffusivity. However, in comparison to the microstructure of CFRP without CNTs the number of voids and bubbles is still too high. That is why the thermal diffusivity is still lower although the CNTs amount is higher and the CNTs distribution is uniform in the epoxy matrix, as shown in fig. 6e.

Also the changes of storage and loss modulus were measured vs. time during the curing of epoxy system without and with different weight fraction of CNTs, as well as solvent addition. The results are shown in fig. 7.
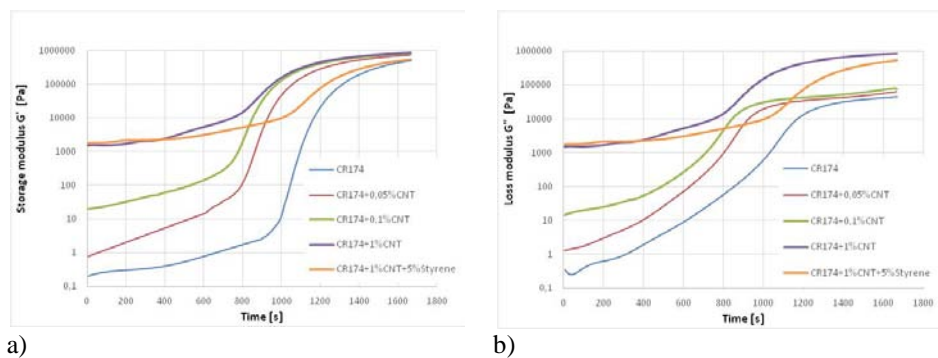

Figure 7. Rheological properties of epoxy system vs. time without and with different amount of CNTs a) storage modulus, b) loss modulus.

Storage modulus G' is specified by ratio of elastic stresses to strain. It expresses the amount of energy remains during shearing process. G' is a measure of the elastic properties of the material. Loss modulus G'' is specified by ratio of viscoelastic stresses to strain. It shows how much energy is dissipated during deformation cycle. G'' is a measure of viscous properties of the material [16, 17]. If the CNTs weight fraction increases in the epoxy system, both storage and loss modulus also increase significantly. Addition of styrene leads to the lower values of G' and G'', what means that the properties are more likely to liquid than solid. In each case G' and G'' values increase vs. time what means that the crosslinking of the epoxy is in progress. From the rheological studies the gel time of the epoxy system was determined as a point where storage and loss modulus crosses, as shown in figs. 8a and b. During the early stage of the reaction G' is below G'' indicating the liquid nature of the material. After some time both G' and G'' increase with the growth of the epoxy chains and their crosllinking. This is followed by a crossover point (gelation point), where the values of G' and G'' are equal. It

means that the system acts as both elastic and viscous, storing and dissipating an identical amount of energy at this point [18, 19].
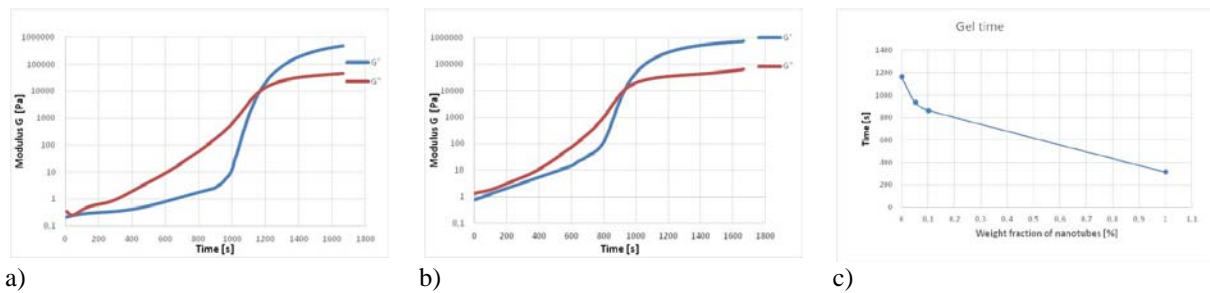

a)   b)   c)

Figure 8. Gel time for: a) epoxy resin system, b) epoxy system with 0.05 wt.% of CNTs, c) as a function of CNTs weight fraction.

The changes of gel time with the addition of CNTs are shown in fig. 8c. Addition of CNTs reduces gel time from 1200 s for epoxy system without CNTs to 360 s for 1 wt.% of CNTs. This speeding up of the process is connected with the increasing of thermal conductivity of the matrix as an effect of CNTs presence. CNTs speed up heat transfer and its uniform distribution in material, what influences on the reaction time.

4. Conclusions

Uniformly dispersed CNTs lead to the significant increase of thermal diffusivity and electrical conductivity of epoxy matrix, however in the case of CFRP laminate the changes are not so obvious. It is caused by the technological reasons. The addition of CNTs influences on the epoxy system (neat resin and curing agent) viscosity. Even a small amount of CNTs significantly increases the viscosity and other rheological properties such as storage and loss modulus. They both significantly increases. Moreover, the addition of CNTs decreases the gel time more than 3 times for 1 wt.% of CNTs. The changes in epoxy system rheology and decreasing of gel time leads to the formation of defect such as voids, bubbles and other structural discontinuities, which can influence the thermal and electrical conductivities.

As it was proved addition of small amount of carbon nanotubes to epoxy resin improves bending strength but only for lower amount of CNTs. When the CNTs weight fraction increases over 0.5 wt.% the bending strength decreases due to defects formation.

Application of solvent during lamination process leads to the decreasing of viscosity and manufacturing of samples without a large number of voids, good impregnation of fibres, what improve the thermal diffusivity. The addition of solvent to the epoxy does not change the electrical conductivity. The temperature decreases the thermal diffusivity of the material.

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