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INFLUENCE OF DICY CRYSTALS ON ELECTRICAL AND MECHANICAL BEHAVIOUR OF THE EPOXY/GLASS COMPOSITE

WPŁYW KRYSZTAŁÓW NA WŁAŚCIWOŚCI ELEKTRYCZNE I MECHANICZNE KOMPOZYTU EPOKSYD/SZKŁO

Abstract: Epoxy/glass composites are widely used in the manufacture of quite a number of electrical machines and equipment. These composites (epoxy/glass laminates) are frequently prepared from prepregs. The prepregs are made by coating woven glass fabric with an epoxy resin, usually cured to the B-stage.
Dicyandiamide (DICY) is used as a curing agent for the epoxy resin. In usual conditions the curing agent is fully depleted during the curing process. However in undesirable conditions DICY crystallizes and these crystals can adversely affect insulation properties of the material.
This paper deals with term specification, when the DICY crystals occur and determination of their influence on mechanical and electrical properties of epoxy/glass laminate. Based on the results is evident that the influence of residual dicyandiamide on electrical properties of epoxy/glass laminate is insignificant.

1. Introduction

Epoxy/glass composites are widely used in the manufacture of quite a number of electrical machines and equipment. These composites (epoxy/glass laminates) are frequently produced from prepregs. The prepregs are made by coating woven glass fabric with an epoxy resin cured to the B-stage.
Dicyandiamide (DICY) is used as a curing agent for the epoxy resin. It contains two amino groups and highly polar cyanimine group.
In usual conditions the curing agent is fully depleted during the curing process. However in undesirable conditions DICY crystallizes and these polar crystals can adversely affect insulating and mechanical properties of materials.

2. Production technology of laminates

The production technology of epoxy/glass laminates can be divided into two stages. In the first stage the prepregs are made, in the second stage the laminates are made from these prepregs by hot pressing.
During a glass cloth impregnation process, composition of impregnating solution is the most important factor.
Because the most of epoxy resins are solid in normal conditions, they are distributed as solutions in a system of organic solvents. This solution is mixed together with curing agent (DICY) and accelerator (i.e. 2-methylimidazol), which is added to increase the speed of chemical reaction.
The full homogenized mixture is loaded into the tank in impregnation line. This line consists of a pre-soaking and soaking roller, soaking tank and a pair of striping rollers. The width of the hole between the striping rollers determinates the thickness of the prepreg.
After the impregnation process the glass cloth continues into the drying tower, where the solvent is vaporized and the prepreg is cured to the B-stage. The degree of cure of the resin can be controlled with the feed speed of the glass cloth or with the temperature in the drying tower.

3. The causes of DICY crystal formation

There are many factors that influence the DICY crystal formation. One of the most important factors is the temperature in the drying tower. The tower is divided into four sections with different temperature values. In the first and second section the temperature is approximately 170°C. Here the impregnated glass cloth is dried and solvents are evaporated. In the third and fourth section the temperature is approximately 180°C. Here the prepreg is cured on required parameters (square weight, viscosity, B-time). If the temperature is higher than limits, the solvent vaporizes too quickly. Viscosity of the solvent affects not only adhesion of resin to glass cloth fibres, but also the proper process of chemical reactions between the components of impregnating solution. The early evaporation of the solvent causes the incomplete depletion of DICY, which precipitates. On the other hand, when the temperature in first two sections is too low, the necessary volume of the solvent does not evaporate and stays in the solution. It is a danger that the impregnating solvent will trickle out of the glass cloth due to the low viscosity. Also the prepreg will contain a higher rate of volatile components (chemicals, witch are released during the pressing process and will bubble the laminate). The amount of solvents and their proportion influence also the DICY crystal formation. The most important solvent is dimethylformamide (DMF). This high boiling organic compound takes effect especially in last two sections of drying tower, where the low boiling solvents (i.e. 1-methoxy-2-propanol) are evaporated. These low boiling solvents take effect in first two sections, where they improve uniform coverage of the glass cloth and adhesion of the resin. If DMF would be the only one solvent in the impregnating solution, its volume wouldn't evaporate during the curing process, which results in increasing of volatile compounds in prepreg. Contrariwise, if the DMF content in the impregnating solution will be lower, the viscosity will decrease early witch can results in DICY crystal precipitation. Other factor, which affects DICY crystal formation in the prepreg, is the feed speed of glass cloth in the impregnation line. If the feed speed is too low, the viscosity of impregnating solution increases in the first part of drying tower due to the evaporation of low boiling solvents. This leads to harder reaction conditions and to DICY precipitation. When the feed speed of cloth is high, some amount of DICY stays in impregnating solution due to the short time of curing. In this regard, the final viscosity of solution will be low and the volume of volatile compounds in prepreg will be higher.

4. Experimental part

4.1 Materials

Three variants of epoxy/glass composite with thickness 0,3 mm and 1 mm was used. The variants differ in the amount of DICY crystals in sample volume as is shown in table 1. The impregnating solution composes of bisphenol A epoxy resin dissolved in methylethylketone with appropriate amount of DICY (hardener) and 2-methyimidazole (accelerator). The 2116 type of glass cloth was used as reinforcement of the composite.

Table 1: DICY crystal content in materials

A	no DICY crystals
B	low amount of DICY crystals
C	high amount of DICY crystals

4.2 Methods

Dissipation factor (tan δ) and relative permittivity (ε_r) at frequencies of 50 Hz and 1 MHz and surface resistivity (σ) were investigated. Automated measuring system LDV-5 was used for the frequency of 50 Hz, Q meter was used for the frequency of 1 MHz. Electrometer Keithley 6517A with resistivity test fixture Model 8009 was used for surface resistivity measurement.

All samples were measured in original condition and after exposition to 50 °C deionized water. Upon removal from hot water, the samples were preconditioned in laboratory environment (23±2 °C and 50±5 % RH) for 24 hours prior to testing.

5. Results and discussion

In original condition all samples behaved very similar and variance of their properties was independent on the amount of DICY crystals, as is shown in table 2 and 3.

Table 2: Results for samples with 0,3 mm thickness in original condition

Material	A	B	C
tg $\delta_{50\ Hz}$	$4{,}5.10^{-3}$	$4{,}4.10^{-3}$	$4{,}0.10^{-3}$
tg $\delta_{1\ MHz}$	$1{,}8.10^{-2}$	$1{,}8.10^{-2}$	$1{,}5.10^{-2}$
σ (Ω)	$1{,}2.10^{16}$	$8{,}2.10^{15}$	$1{,}8.10^{16}$

Table 3: Results for samples with 1 mm thickness in original condition

Material	A	B	C
tg $\delta_{50\ Hz}$	$4{,}0.10^{-3}$	$4{,}0.10^{-3}$	$4{,}0.10^{-3}$
tg $\delta_{1\ MHz}$	$2{,}0.10^{-2}$	$2{,}1.10^{-2}$	$1{,}9.10^{-2}$
σ (Ω)	$2{,}5.10^{15}$	$2{,}0.10^{15}$	$3{,}1.10^{16}$

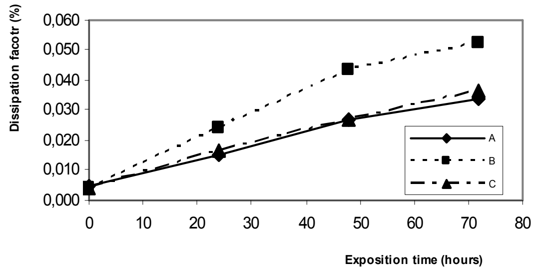

Figure 2: Dependence of dissipation factor on the time of exposition to water (50 Hz; 0,3 mm)

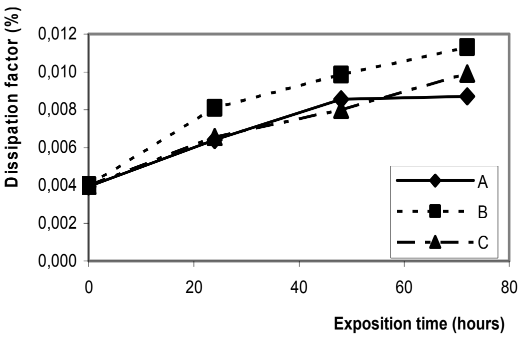

Figure 3: Dependence of dissipation factor on the time of exposition to water (50 Hz; 1 mm)

After exposition to water the dissipation factor of all three materials at frequency of 50 Hz increases in dependence to exposition time as is shown in figures 2 and 3. It is curious that tan δ of the material with low content of DICY crystals had increased noticeably, while tan δ of the material with high content of DICY crystals behave similar to the material with no content of residual hardener. At frequency of 1 MHz behave all materials similar (figures 4 and 5).

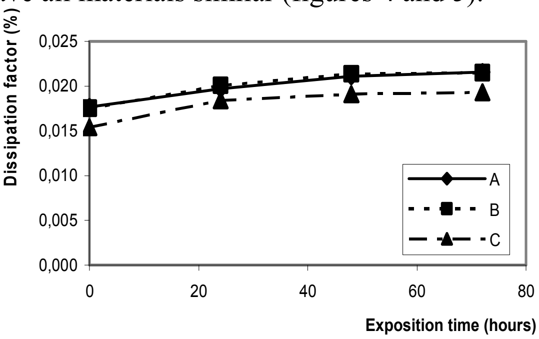

Figure 4: Dependence of dissipation factor on the time of exposition to water (50 Hz; 0,3 mm)

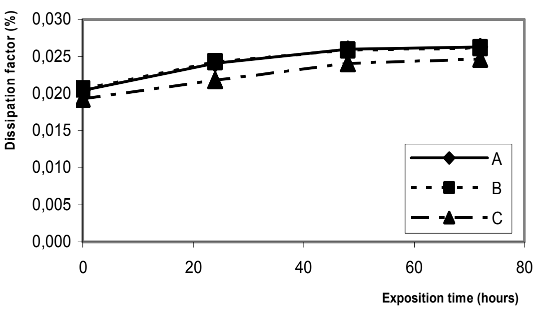

Figure 5: Dependence of dissipation factor on the time of exposition to water (1 MHz; 1 mm)

An impact of DICY crystals on surface resistivity of materials is also unconvincing. There is a rapid fall of surface resistivity after 24 hours exposition by all three materials. Decrease in resistivity continues with increasing time down to the values of 10^{15} Ω, which is shown in figures 6 and 7.

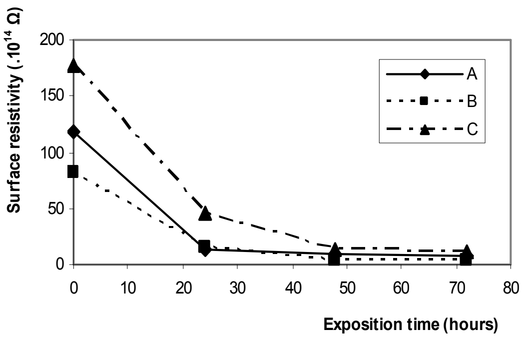

Figure 6: Dependence of surface resistivity on the time of exposition to water (0,3 mm)

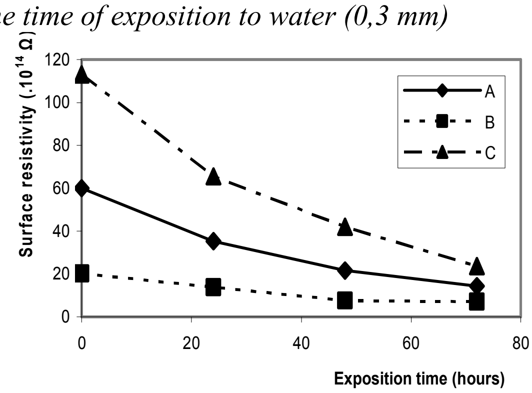

Figure 7: Dependence of surface resistivity on the time of exposition to water (1 mm)

Based on the results of the experiment it is evident that the influence of residual dicyandiamide on electrical properties of epoxy/glass laminate is insignificant.

6. Acknowledgment

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7. Literature

[1]. JACKSON M.L., LOVE B.J., *Dicyandiamide precipitation in epoxy solutions and latex dispersions: threshold concentration analysis using a two-stage drying model*, Polymer, Volume 45, Issue 21, 2004, Pages 7229-7238

[2]. ONDRÁČEK M., KUČEROVÁ E., *Vliv impregnace tenkých skleněných tkanin na elektrické vlastnosti laminátů* [diploma thesis], Plzeň, 2006

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