The Influence of Curing Conditions on Properties of Electrically Conductive Adhesives

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Anotace:
Práce se věnuje problematice elektricky vodivých lepidel, která se používají jako alternativa k pájeným spojům. Práce je zaměřena na analýzu vlivu podmínek vytvrzování na elektrické a mechanické vlastnosti elektricky vodivých lepidel. Vzorky spojů vytvořených elektricky vodivým lepením byly vytvrzovány jednak za podmínek doporučených výrobcem ale také v prodloužených časech. Průběžně byly sledovány změny parametrů spojů v průběhu času vytvrzování. Měřily se parametry jako elektrický odpor a střihová síla lepených spojů. Byl také analyzován vliv různých doporučených kombinací podmínek vytvrzování. Jev dodatečného vytvrzení byl zjištěn během prodloužené doby vytvrzování.

The work is focused on problematic of electrically conductive adhesives. These are used as an alternative to solder joints. Goal of work was concentrated to analysis of influence of curing conditions on electric and mechanical properties of electrically conductive adhesives. Samples of joins realized by electrically conductive adhesives were cured at conditions recommended by producer as well as in extended time. Changes in parameters over time have been monitored continuously. Electrical resistance and tear out force of adhesive joints were measured. Influence of different recommended curing conditions was analyzed too. The effect of post-curing or degradation of binders may appear during curing process.

INTRODUCTION

Electrically conductive adhesives are used as alternative to soldering technology. The biggest boom of adhesive came after the issue of The EU's Restriction of Hazardous Substances (RoHS) Directive in 2006. It was necessary to find a substitute for lead solder due to the restriction of lead in electronics. Electrically conductive adhesives have a number of disadvantages, but despite this they have irreplaceable applications. Some components such as LCD display would be damaged during soldering due to higher temperature. Curing temperatures of electrically conductive adhesives are significantly lower than the melting temperatures of commonly used soldering alloys.

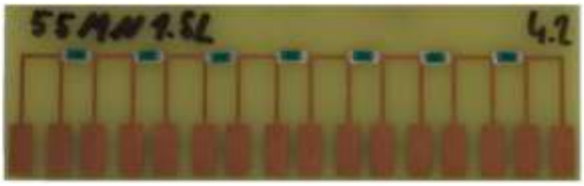
THE SAMPLES

The samples with one and two components electrically conductive adhesives filed by silver fy AMEPOX were prepared. Information on adhesives is summarized in table 1. Adhesive were cured under

Tab. 1: Adhesives used for sample preparation

Type of adhesive	Number of components	Percentage of silver	Curing conditions in air circulated oven
ELPOX AX 12 LVT	two	55%	80°C – 25 min 100°C – 15 min 120°C – 10 min 20°C – 24 hours (*)
ECO SOLDER AX 70MN	one	70%	150°C – 20 min (*) 180°C – 9 min 200°C – 4 min 20°C – 24 hours (*)
ELPOX ER 55MN	one	70%	150°C – 20 min 180°C – 8 min 200°C – 4 min 20°C – 24 hours (*)
(*) Curing conditions added outside the producer's recommendations			

conditions recommended by producer. Producer offer alternative conditions. Some samples were prepared at additional conditions outside the producer's recommendations. Some samples were not cured in oven at increased temperature and were left at room temperature several hours. Combination of 150°C – 20 min for adhesive AX 70MN was added for comparison with adhesive ER 55MN. These non-standard conditions are marked as (*) in tab. 1. Used one component adhesives contain epoxy-phenolic resin binder, two component adhesive AX 12LVT contain epoxy base.

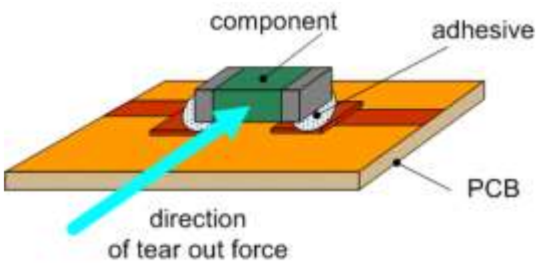


Obr. 1: Sample for testing of adhesive joins

Example of tested sample is shown in fig. 1. The smd resistors with "zero" resistance are placed on composite FR4 board with cooper foil. Resistors are fixed to board by electrically conductive adhesive. Adhesive was deposited to pads by stencil printing to ensure a constant amount of adhesive. Samples were subsequently cured in air-circulated oven.

PARAMETERS OF ADHESIVE JOINS

Electric resistance was one of tested parameters of adhesive joins. Resistance was measured by 4-wire methods with using of miliohmeter. Mechanical properties there represent the force in the shear. Tear out force required to break the resistance from the board was measure by vertical breaker. The force is acting from side of resistor as the fig. 2 shows.

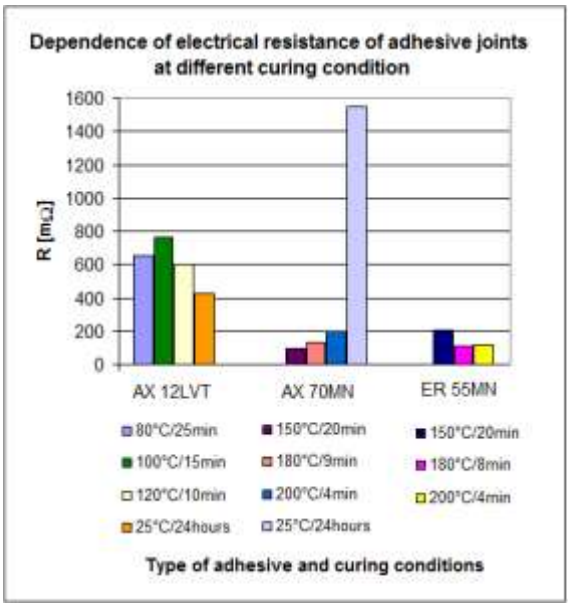


Obr. 2: tear out of glued component

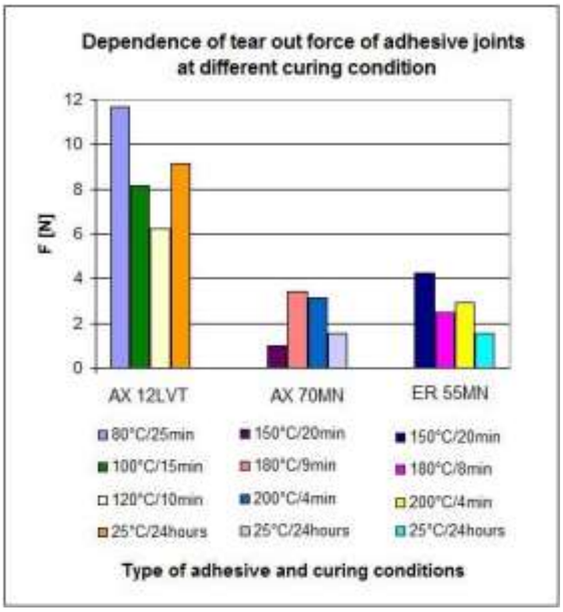
RESULT DISCUSSION

Influence of curing conditions

The influence of curing conditions was analyzed. Producer recommends alternative conditions for curing for adhesives used in our experiment. Graphs in fig. 3and 4 show values of electrical resistance and tear out force for tested adhesives at different curing temperatures and times.



Obr. 3: Resistance of adhesives at different curing conditions



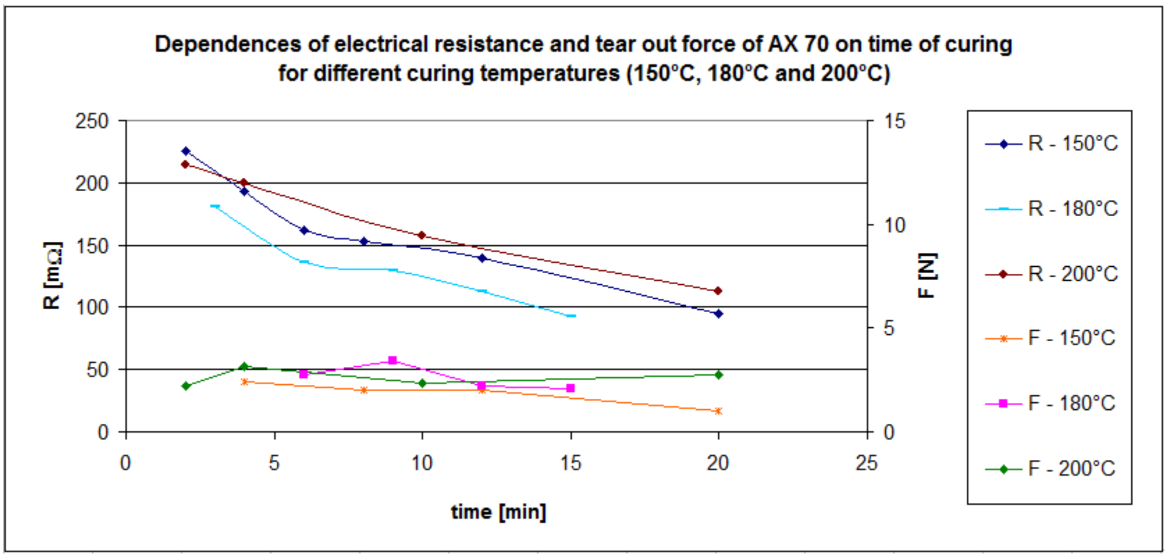
Obr. 4: Tear out force of adhesives at different curing conditions

Significantly different behavior is observed for two component adhesive compared to one component adhesives. Resistance of joins realized by two component adhesive AX 12 is approximately 5 times higher than for one component adhesives in general. On the contrary AX 12 is better from the point of view of mechanical strength. Measured forces for AX are 3 times higher on average. Adhesive AX 12 has

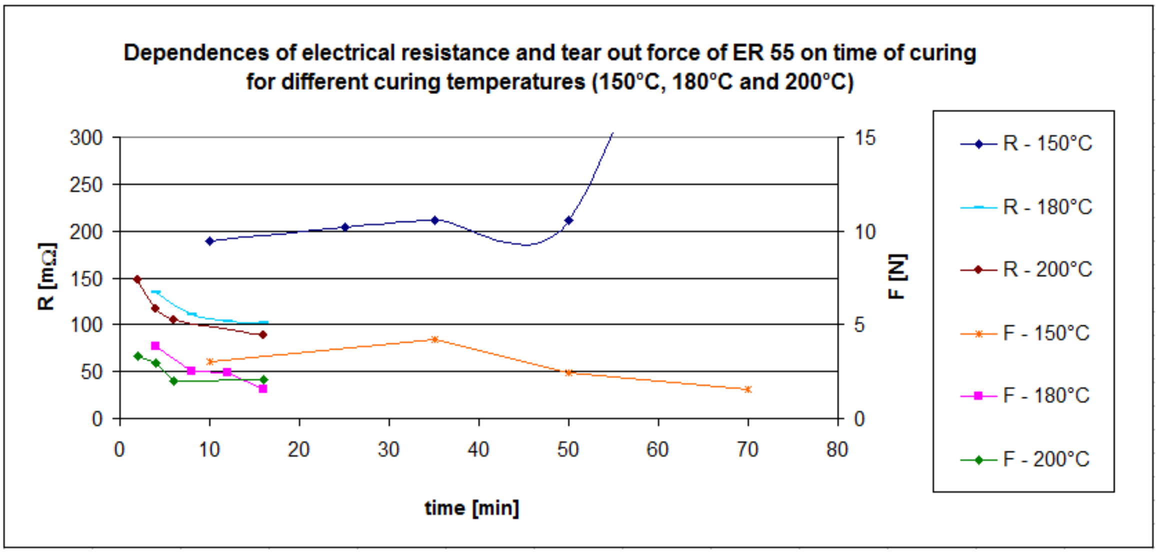
the lower ratio of conductive silver particles – see tab. 1. Higher amount of binder is enhanced the mechanical properties but on the other hand is worsen the conductivity. More conductive bridges for current flow are created in structure with high content of conductive particles.
Curing at 150°C /20 minutes was realized in addition to adhesive AX 70 for comparison with adhesive ER 55. From graph in figs. 3 and 4 we can see that curing condition is inappropriate. Value of electrical resistance is low but tear out force is very low, even lower than for samples "cured" at room temperature. Electrical resistance of joins realized by adhesives non cured at enhanced temperature (25°C) reach very high values. That resistance is 10 times higher than for samples cured at enhanced temperatures (150°C, 180°C and 200°C). Significant shrinkage of binder does not occur at room temperature and silver particles are separated from each other mostly.
Electrical resistance of joins realized by adhesive ER 55 left at room temperature was not measurable. Curing at 150°C and 25 minutes seems to be the worst. Resistance of joins is almost two times higher than for other two conditions. On the contrary the shear force is lower. Force for samples "cured" at room temperature was measured too for comparison. Graphs in figs. 3 and 4 indicate that is possible reach better properties of joins at higher curing temperature.

Post-curing of adhesives

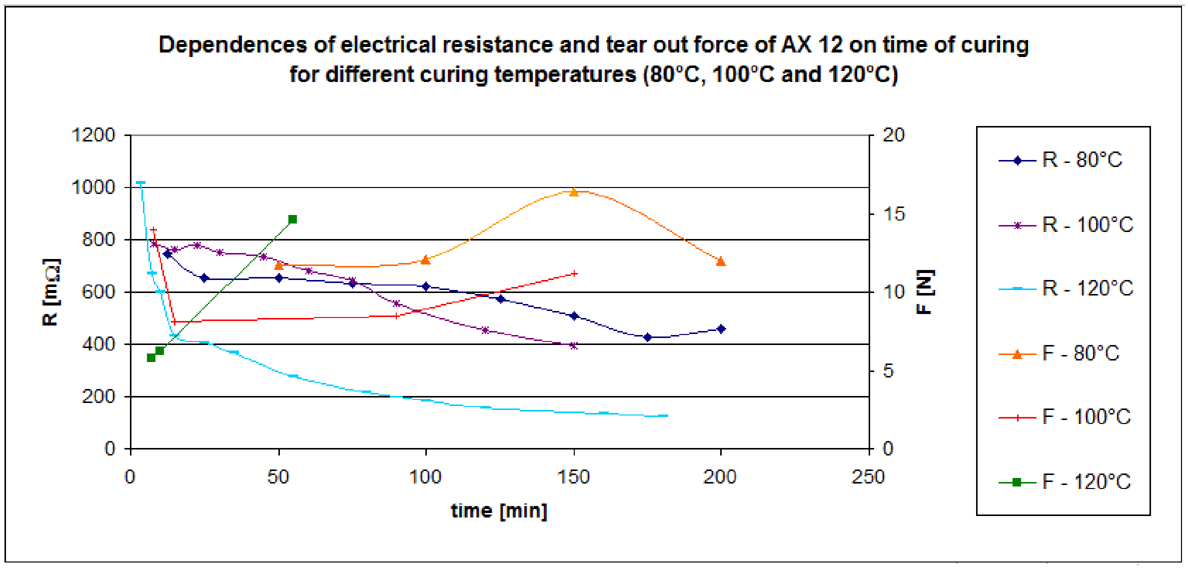
Changes of properties of electrically conductive adhesives in dependence on time of curing were analyzed too. Samples with adhesives cured during insufficient time were measured. Furthermore the samples cured longer time than give the recommendation of producer. Dependences of electrical resistance and tear out force of tested adhesives on time of curing is shown in figs. 5, 6 and 7. Post-curing effect often occurs with electrically conductive adhesives [1, 2].
Fig. 5 shows dependence of parameters on curing time for adhesive ER 55. Dependence for curing temperature of 150°C has an unexpected progression. Best properties are reached at uncured state after short time that is half of recommended time. Decreasing of parameters is observed with longer time. Progress of force is not in accordance with assumption. Non standard behavior can cause adhesive out of expiration date. A big change occurs in time about 50 minutes when the electrical resistance rises rapidly and force is decreasing too. This suggests that degradation in adhesion was started. Electrical resistance of adhesive joins is larger for uncured samples for curing temperatures 180°C and 200°C in times shorter than recommended. From graph in fig. 5 we can see that resistance is decreasing when time of action of enhanced temperature is prolonged. That indicated the post-curing effect.
Dependence of resistance of adhesive AX 70 for all curing temperatures predicates the post-curing effect as show graph in fig.6. Even here the conductivity of joins is improved at longer curing time than recommended time. Tear out force does not change significantly. Anomalies in dependencies are most likely caused by an error resulting from a relatively small number of samples to measure the tear out force.
Graph in fig. 7 is shown the dependence of electrical resistance and tear out force on curing time for adhesive AX 12. Rapid change of resistance is observable between samples cured at short time and the samples cured at recommended time. Resistance



Obr. 5: Dependences of electrical resistance and tear out force of AX 70 on time of curing



Obr. 6: Dependences of electrical resistance and tear out force of ER 55 on time of curing



Obr. 7: Dependences of electrical resistance and tear out force of AX 12 on time of curing

is more stable for samples cured for longer periods than recommended. A greater drop in resistance value occurs in times about 3-4 times longer than the recommended curing time. Noticeably growth of force of samples cured in these long time can be seen from graph in fig. 7. Of course these value fluctuations could be caused by relatively small number of samples to measure the tear out force. But this phenomenon is observed for all curing temperatures. Reason of this behavior could be some change in structure exposed to a longer period of enhanced temperature. Post-curing effect is observed for adhesive AX 12 too.

CONCLUSION

Analyzed dependencies indicate that adhesive AX 12 appears to be the best at long-term cure at room temperature. The structure stabilizes over a long period of time. Due to the nature of the adhesive, the structure is cured without difficulty even at room temperature.

But for standard recommended curing conditions the results can indicate that use of higher curing temperature has a favorable effect on properties of adhesive join. This may be due to a higher speed of evaporation of the hardener from the adhesive.

Micro-holes then close before the macromolecular spatial network is created.

Post-curing effect was observed for all tested adhesives. Electrical resistance did not stabilize at curing time longer than recommended. Resistance was decreased with curing time in most causes. Degradation of adhesive can start during long-term exposure to enhanced temperature. Degradation was detected for adhesive ER 55 cured at 150°C 50 minutes only. For other curing conditions and adhesives has not been reached time to degradation. Maximum of tear out force was reached for samples cured at recommended condition for one component adhesives. Two components adhesive has a slightly different progress of curing process. This is due to different type of binder and also lower curing temperatures have to be into consideration.

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