INFLUENCE OF THE HARDENER PROPORTION ON MECHANICAL PROPERTIES OF ADHESIVE BONDS USED IN AGRICULTURE*

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Joining materials by adhesive bonding is used across all industrial branches. The occurrence of adhesive bonds in machine constructions is still more frequent because of the development of adhesives which are able to meet various requirements of designers. This trend is observable also in agriculture – in the construction of agricultural machines. There even exists a co-operation between the companies developing the adhesives and the agricultural machines producers. The production process of machines and equipment must consider a required production tact. Adhesives and the process of their hardening have to meet these requirements. In the sphere of agriculture, epoxy resins hardening based either on hardeners or heating are used. Mechanical properties of two-component epoxy resins depending on variable amount of the hardener starting crosslinking of these reactoplastics are described.

adhesive bond; epoxy resin; temperature; tensile strength

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INTRODUCTION

The adhesive bonding technology belongs among methods of heatless materials joining. It is a progressively developing method applicable also in agriculture. Adhesives, apart from being used for joining materials in constructions of agricultural machines and equipment, can also serve as the matrix of composites (e.g. reactoplastics serve as a matrix for fibre and particle composites) utilizable for machines renovation in agrocomplex (Valášek, Müller, 2013a; Valášek, Müller, 2013b). Another example of adhesives usage is efficient joining of materials based on technical ceramics. Technical ceramics is one of possibilities to increase wear resistance in tools serving for soil processing (Müller et al., 2013). Adhesive bonding technology is an effective method easily implementable in a piece-production as well as in serial production (Messler, 2004; Sargent, 2005). An important aspect of the adhesive bond is an adherent treatment before putting the adhesive when it is necessary to ensure optimum wetting of the surface by a suitably chosen adhesive. Also epoxy adhesives are used in agriculture (Doyle, Pethrick, 2009; Grant et al., 2009; Liljedahl et al., 2009). Mechanical properties of epoxy resins and their ability to resist to various types of contaminants speak in favour of their application. In agriculture adhesive bonds can be exposed to environment, which may cause an undesirable modification of the adhesive in time – degradation, owing to the character of conditions (Müller, Valášek, 2012; Müller, Herák, 2013). A product of alkaline condensation of dian (Bisphenol A) with epichlorhydrin can be marked as one of the most commonly used epoxy resins (a resin of glycidyl type). Epoxy resins are prepared with different molecular masses. It is generally said the less amount of epichlorhydrin comes to 1 mol of dian the higher the resultant molecular mass of the resin is (chemical resistance increases with the molecular mass). A certain ratio of

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Table 1. Example of used ratious of hardener to 100 parts of resin

Specification	60%	70%	80%	90%	100%	110%	120%	130%	140%
Parts of hardener	3.90	4.55	5.20	5.85	6.50	7.15	7.8	8.45	9.10

the hardener which starts the crosslinking – creation of bonds in macromolecular chains – is necessary for the resin hardening. Hardening of epoxy resins by polyamins at normal temperatures lasting for a relatively short time is already in progress, however, the used polyamin should necessarily have at least three active atoms of hydrogen in the molecule. A reaction is in progress at creating hydroxyl and amine group (Equation 1) (M l e z i v a , 1993):

$$R—NH_2 + CH_2—CH— \Rightarrow R—NH—CH_2—\overset{OH}{\overset{|}{C}}H— \quad (1)$$

Theoretically the requested amount of hardener is defined from an epoxy equivalent of the used resin (a mass (g) of the resin containing 1 mol of epoxy equivalent) and an amin equivalent of relevant polyamin (molecular mass of polyamin divided by a number of active amin hydrogens). 10% of the hardener surplus is used in the practice – the used polyamin is not 100%. According to the producers, a greater proportion of the hardener can lead to the decrease of mechanical properties in a number of epoxy adhesives (M l e z i v a , 1993).

The aim of the experiment is to define the influence of the hardener amount on mechanical properties of adhesive bonds and the time of its processability. A hypothesis can be uttered that the producers do not give the optimum ratio of the hardener. The reason is a presumptive speculation on the speed of processability time. It is important to respect the production tact (processability time of the mixture after adding the hardener) at keeping the mechanical properties at application of the epoxy adhesives not only in the production of agricultural machines.

The paper describes shear strength of rigid overlapped samples, cohesive strength of the adhesive which is defined by means of the tensile strength of universal test samples, and furthermore the hardness of hardened epoxy adhesives.

MATERIAL AND METHODS

A two-component epoxy adhesive ChS Epoxy 1200/371 (DCH-Sincolor, a.s.,Pilsen, Czech Republic) (medium-molecular epoxy adhesive modified by an unreactive softener) was used in the experiment. Diethylentriamin – hardener P11 ((DCH-Sincolor, a.s.,Pilsen, Czech Republic) was used for resin hardening. The producer recommends the ratio of 100 parts of the resin to 6.5 parts of the hardener (100%) to be applied for hardening and declares the processability time of 26 min and the gelatation time of 60 min. Full strength of the adhesive bond at using the mentioned hardener and the ratio stated by the producer should be reached after 7 days.

Test samples containing a different hardener/resin ratio (60–140%, while 100% is the ratio stated by the producer) were prepared (Table 1).

The hardener and the resin were mechanically mixed. This mixture was subsequently used for the production of test samples – casting into prepared forms, creation of overlapped bonds. The test samples were prepared also in various time intervals from the preparation of the mixture except for observing mechanical properties depending on the amount of the hardener used for hardening. The temperature of the adhesive was measured regularly at the same time intervals by means of an infrared thermometer Testo 845 (Testo, s.r.o., Prague, Czech Republic) during this procedure.

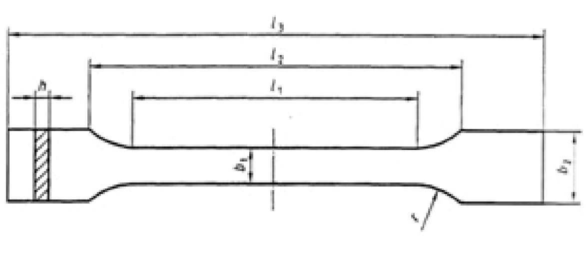


Fig. 1 Multipurpose test sample – Tensile strength (C S N E N I S O 3 1 6 7 , 2004)

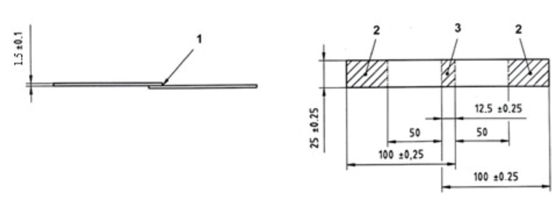


Fig. 2 Test specimen – Lap-shear tensile strength (CSN EN 1465, 1997)

1-bonded joint, 2-adherent (steel sheet), 3-epoxy resin

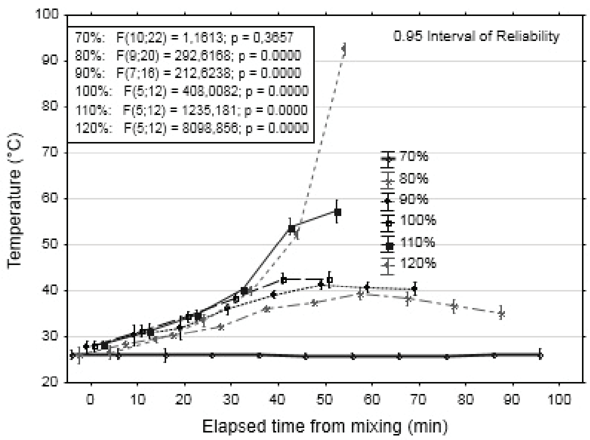


Fig. 3 Initiation of heat depending on time pause from moment of mixing of hardener and resin

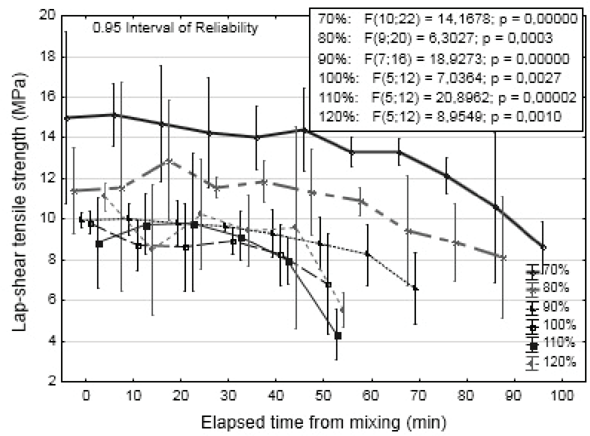


Fig. 4 Dependence of lap-shear tensile strength on time pause from moment of mixing of hardener and resin

Laboratory tests

The test samples determined for the specification of cohesive strength by means of tensile strength were prepared according to the requirements of the standard CSN EN ISO 3167. The test specimens were tested on a universal testing machine. The speed of the cross beam motion was 6 mm·min^{-1}. The setting of the tensile characteristics was performed in accordance with the standard CSN EN ISO 527 (Fig. 1).

For the lap-shear strength description at the boundary adherent–filled system the overlapped assemblies were made (CSN EN 1465) (see Fig. 2). The surface of 1.5 mm thick steel sheets (S235J0), onto which the composite system was applied, was at first blasted using the synthetic corundum of the fraction F80 under the angle of 90°. In this way the average surface roughness Ra = 2.11 µm was reached. Then the surface was cleaned and degreased using Aceton P6401 and prepared for the composite mixture application. The bond width was defined using distant wires of 0.15 mm in diameter.

The fracture of the surface and adhesive layers was evaluated using a stereoscopic microscope. Statistical evaluation of the results was carried out by means of the STATISTICA (Version 12, 2013) software package – One Way ANOVA, reliability level $\alpha = 0.05$. For statistical comparison the *t*-test was used when the zero hypothesis H_0 ($P > 0.05$) stated an agreement of the statistical sets of data.

RESULTS

Test samples were prepared in the laboratory at the temperature 23 ± 2°C. During the test samples preparation, the heat released into the environment during the resin crosslinking by the hardener was measured (Fig. 3). The producer declares the processing time of 26 min. However, the mixture was theoretically applicable also after passing that time.

The dependence of the amount of released heat on the amount of the hardener used for hardening is obvious from Fig. 3. Peak temperature of the mixture did not exceed 42.8°C (after 40 min) at the ratio of the hardener given by the producer (100%). At 120% of the hardener the peak temperature was 92.6°C (50 min), at 70% of the hardener it was only 26.2°C (10 min). The temperature in the graph (Fig. 3) was measured at the time of applicability and it was changing with a varying amount of the hardener.

The temperature of the hardener and resin mixture varied depending on the amount of the hardener and the time from the moment of their mixing. Shear strength of rigid adherents (CSN EN 1465), whose bond was created (that means the adhesive was put on adhesive bonded part 1 and closed with adhesive bonded part 2) at different time intervals from the moment of mixing a variable amount of the hardener and the resin, was evaluated at the same time (Fig. 4).

The time of the mixture processability is 26 min after adding the hardener. It is obvious from Fig. 4 that the decrease of shear strength occurred after this time at all concentrations of the hardener. The influence of the filler amount is also obvious. A cut through the tested adhesive bond is presented in Fig. 5.

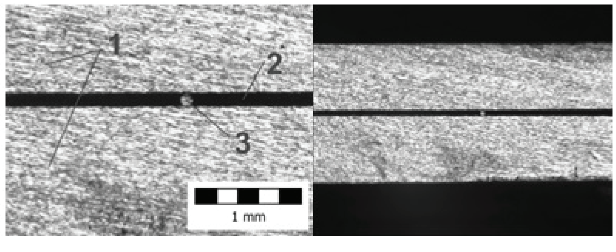
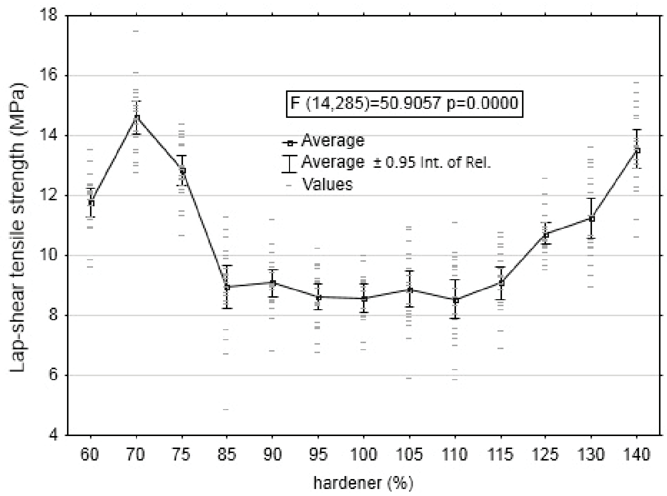
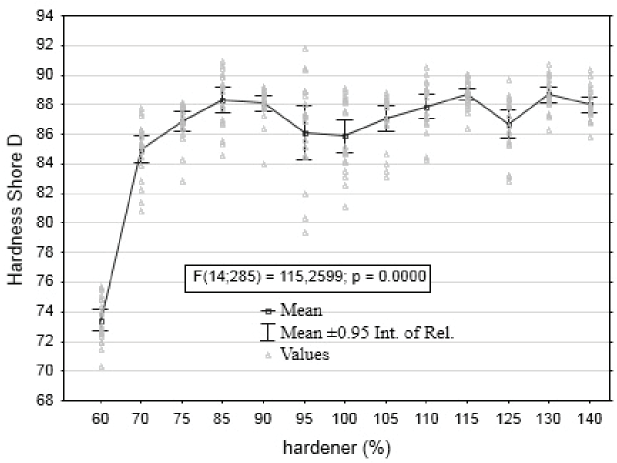


Fig. 5 Cut through adhesive bond – 1-adherent, 2-epoxy resin, 3-distance wire



Lap-shear tensile strength						
%	mean (MPa)	agreement				
110	8,55	*				
100	8,57	*				
95	8,63	*				
105	8,88	*				
85	8,95	*				
90	9,07	*				
115	9,09	*				
125	10,74		*			
130	11,23		*			
60	11,78		*	*		
75	12,84			*	*	
140	13,55				*	*
70	14,61					*

Fig. 6 Dependence of lap-shear tensile strength on amount of hardener, Anova - Tukey´s HSD test



Hardness							
%	Shore D	agreement					
60	73,41	*					
70	85,00		*	*			
100	85,88		*	*	*		
95	86,07		*	*	*	*	
125	86,68		*	*	*	*	*
75	86,88		*	*	*	*	*
105	87,07				*	*	*
110	87,88				*	*	*
140	88,01					*	*
90	88,09					*	*
85	88,30						*
130	88,68						*
115	88,70						*

Fig. 7 Dependence of hardness on amount of hardener

Shear strength was also determined at keeping a constant time interval from the mixture preparation, however, with a variable amount of the hardener (Fig. 6). Tukey's HSD test was used for the statistical evaluation (Fig. 6 right). The highest (16.55%) range of the measured values was observed by the 85% hardener ratio (at 100% the variation coefficient equalled 11.66%).

Test samples for evaluation of hardness and tensile strength were cast into forms made of Lukopren N (Lučební závody a.s., Kolín, Czech Republic). Hardness of the cast samples hardened according to the producer's requirements but with a variable ratio of the hardener was measured after 7 days (Fig. 7). Generally it can be said that a smaller proportion of the hardener led to lower hardness. The hardness value increased with increasing ratio of the hardener. Hardness stabilized around the value 88 Shore D (see the statistical evaluation in Tukey's HSD test – Fig. 7 right). The variation coefficient did not exceed 5% at measuring the hardness.

Cast test samples were also tensile tested. The aim of the tensile test was to describe the cohesive strength depending on a variable ratio of the hardener. It is a significant factor at the application in the area of bonding methods. Fig. 8 shows tensile strength together with an elongation.

The increase of the tensile strength with increasing ratio of the hardener is visible from the measured values, the increase of values was stabilized from 120%.

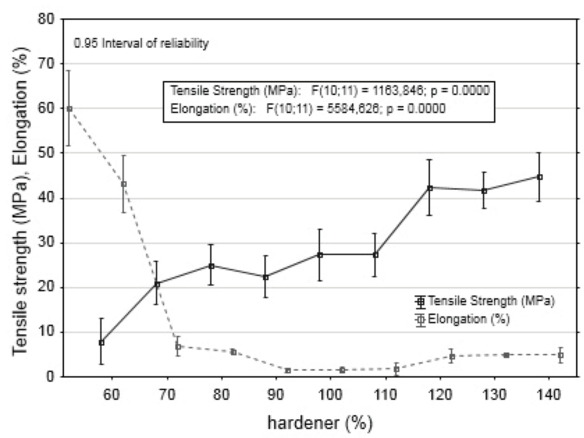


Fig. 8 Dependence of tensile strength and elongation on amount of hardener

Elongation values were high at using a small ratio of the hardener. The values decreased step by step, strong fall finished on the line 70% of the hardener and then it became stabilized. Variation coefficient did not exceed 10%. Increasing of the cohesive strength above 100% of the hardener is in accordance with the statement of Mleziva (1993) about effecive utilization of 10% of the filler surplus. The effecive surplus of observed adhesive falls within the interval 10–20%.

DISCUSSION

The experiment confirmed that mechanical properties of the resin are influenced by the mutual ratio of the hardener and the resin in the mixture. It came to a 70% increase of shear strength at systems with a 70% proportion of the hardener, and to a 58% increase of shear strength at systems with 140% of the hardener compared with the mixing ratio recommended by the producer. The highest tensile strength was reached at the system with the hardener ratio increased by 140–64% compared to the ratio stated by the producer.

The adhesive bonds strength is a common subject of laboratory experiments. It is influenced by a number of factors such as processability time, treatment of the adhesive bonded surface, hardening process, and degradation aspects influencing the service life of the bond (Müller, Herák, 2010). The reproducibility of experiments is key for their results. From the performed experiment it is obvious that at all series of the test samples the same proportion of the hardener has to be kept to ensure mutually comparable results.

CONCLUSION

From the experiment results it can be concluded that:

• Lower amount of the hardener is suitable for bonds where a significant deformation is presumed. The deformation can be caused by stress of the adherent in the area of elastic deformation, by heat-tensibility. The deformation increased 75 times in the interval 60–70% of the hardener – adhesive bonds showed an adhesive type of failure. However, the adhesive tensile strength decreased by 30% in this interval. The adhesive bond strength was, however, higher in this interval comparing with the hardener ratio stated by the producer. This state can be caused by the interaction of the adhesive and the adherent at their mutual deformation.

• The hardness Shore D is steady in the interval 70–140% of the hardener. It follows from the results that the amount of the hardener in this interval does not influence hardness. The value of hardness Shore D significantly decreased in the case of the hardener amount decrease below 70%. The difference between maximum and minimum reached hardness is 70%.

• Temperature after the resin and hardener mixing significantly increases in the interval 110–120%. A significant increase of temperature occurs after 30 min from processing.

• Processability time of mixed adhesive increases at the application of the hardener in the interval 70–90%.

• Cohesive strength of the tested adhesive increases with increasing ratio of the hardener (up to the tested value of 120%).

• Adhesive strength of the adhesive bond increases in the interval 70–90% of the hardener, that means better adhesion to the adhesive bonded material is reached.

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