

Ethyl acetoacetate as a formaldehyde scavenger in UF resins used to bond beech veneer

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Abstract: *Ethyl acetoacetate as a formaldehyde scavenger in UF resins used to bond beech veneer.* The study investigated the possibility of using acetoacetate groups to reduce the emission of formaldehyde from plywood glued with UF resin. Ethyl acetoacetate (in amounts of 5, 10 and 15%) was applied to the veneers, prior to the bonding process with UF resin, and then subjected to esterification at different temperatures (20, 40 and 60°C). Studies have shown that the use of acetoacetate groups enables significant, even a 66% reduction in formaldehyde emissions from plywood, in the case of esterification process at a temperature of 40°C.

Keywords: acetoacetate groups, formaldehyde, UF resin, plywood

INTRODUCTION

An interesting way to reduce of formaldehyde (HCHO) emissions from materials containing amino resins is the introduction of substances containing acetoacetate groups (acac). They demonstrate the ability of the reaction with hydroxyl group in aminoplast and aldehydes, including formaldehyde (Del Rector et al. 1989). The first attempts to use the acac groups in particleboard industry as sorbent of free formaldehyde have made Sellers et al. (1990). Also in the Department of Wood-Based Materials investigated the effect of compounds containing the acac groups on HCHO content and physical and mechanical properties of particleboard glued with urea-formaldehyde resin (UF) (Dziurka et al. 2003 and 2004). The research have shown that regardless of the way of the introduction of these groups, on chips or directly to the resin, or the form of the compound, pure ethyl acetoacetate or emulsions grafted with acetoactate groups, the lowering of the contents and emissions of formaldehyde, while maintaining adequate physical and mechanical properties produced boards were observed.

There is, however, no reports on the use of such compounds in the production of plywood, glued with UF resin. The problem is important due to the fact that in the manufacture of plywood must be applied the resin with higher ratio of F/U. However, the higher ratio of F/U the higher emissions of formaldehyde.

Therefore, in this study, as a formaldehyde scavenger in UF resin for manufacturing of plywood, it was decided to use ethyl acetoacetate.

MATERIALS AND METHODS

Based on our previous studies the ethyl acetoacetate (AcAcEt) during the plywood manufacturing process was applied to the inner veneer in the amount of 5, 10 and 15%, in relation to its dry weight and then were subjected to esterification at 20°C, 40°C and 60°C for 30 min (Dziurka et al. 2003). The glue mixture solution used to join the veneers was prepared according to the manufacturer's recipe plywood, except that urea was not added. It is known

that, in industrial conditions, it is added to bound parts of the formaldehyde. The adhesive mixture was applied in the amount of 160 g/m². The open time of the final set was 5 min. The pressing parameters of plywood were as follows: pressing temperature 120°C, pressure 1.5 MPa, pressing time 1 minute on 1 mm thick of plywood after pressing (about 4 minutes). Emission of formaldehyde was determined by the bottle method, according to PN-EN 717:3.

RESULTS AND DISCUSSION

The results of the amount of ethyl acetoacetate spread onto the veneers on the effectiveness of limitation of the emission of formaldehyde from produced with their used plywood are shown on Figs. 1 and 2.

They showed that increasing the amount of applied to the veneers AcAcEt causes HCHO emission decrease, even up to 66% for its maximum quantity (Fig. 1). This is probably the result of the ability of acetoacetate groups to react with formaldehyde and bound it to chemically resistant methylene bridges form (Del Rector et al. 1989, Dziurka et al. 2003 and 2004).

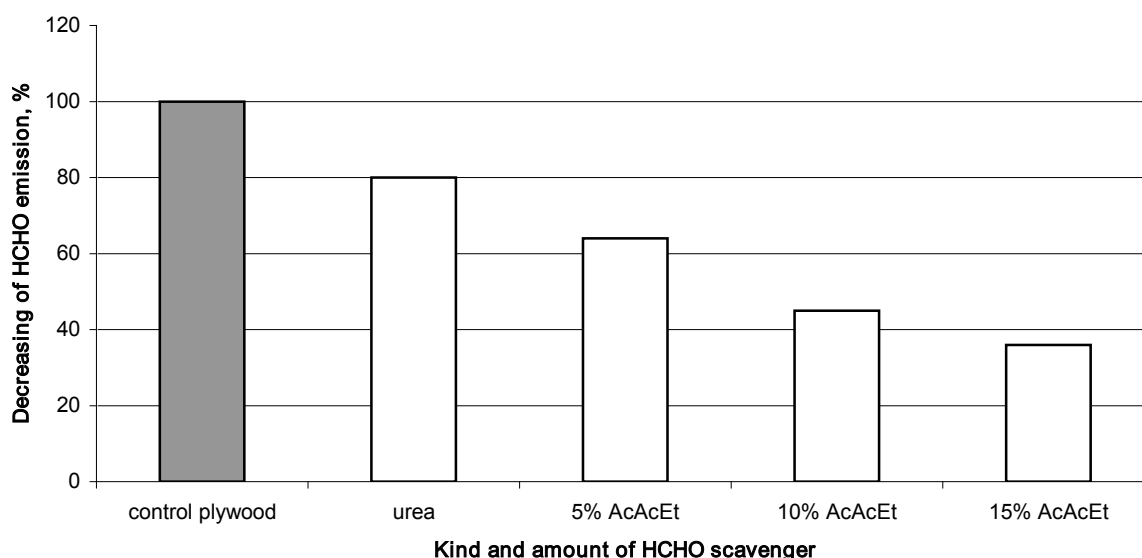


Fig. 1. The effect of the amount of ethyl acetoacetate on the effectiveness of limitation of the emission of formaldehyde from plywood

Under the industrial conditions in order to reduce the emission of formaldehyde to the standard adhesive mixture the urea is added. However, the results of the carried out studies showed that its addition to glue mixture caused reducing emissions of HCHO only about 20%, while in the case of acac groups the result is over 3 times better (66%). This confirms earlier reports about high effectiveness of the acetoacetate groups in bonding of formaldehyde.

The effect of the temperature of veneer acetoacetylation on the effectiveness of limiting formaldehyde emission from plywood is illustrated on Fig. 2. As can be seen from the figure, the formaldehyde emission increases along with the increase of the temperature of acetoacetylation of veneer before gluing. It may be explained by the fact that at higher temperatures two parallel processes occur: a partial decomposition of acetoacetyl groups and their reaction with copolymers of wood, which in effect limits their ability for the reaction with free formaldehyde (Del Rector et al. 1989). The plywoods exhibiting the lowest emission of formaldehyde were obtained when the veneers with ethyl acetoacetate spread on them were not subjected to the action of the raised temperature (20°C). In this case emission of HCHO

was limited to the value that characterizes some natural wood species (Meyer i Boehme 1997, Tsapuk 1992).

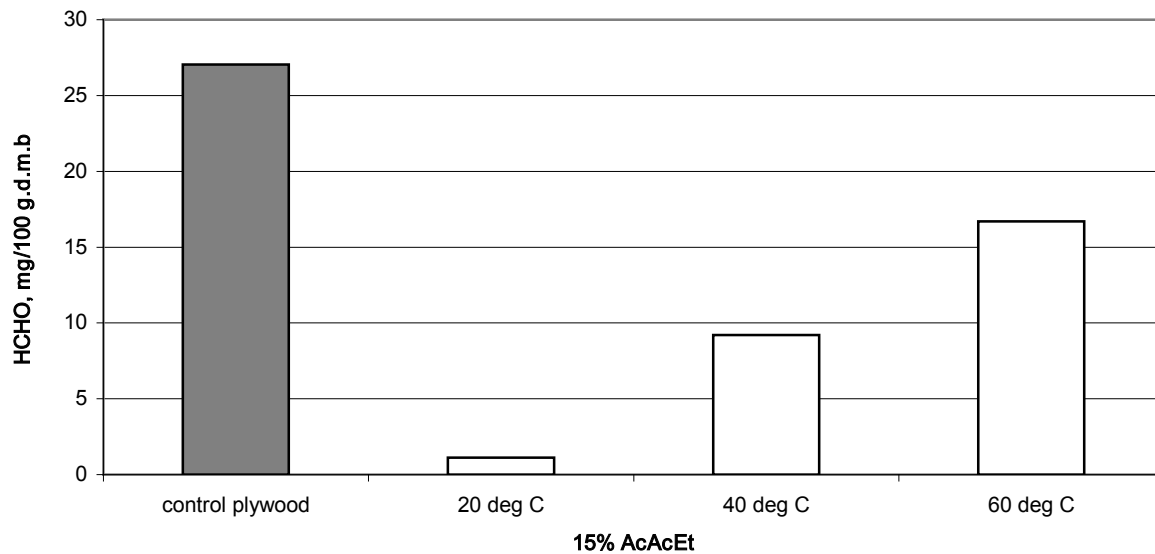


Fig. 2. The effect of the temperature of veneer acetoacetylation on the effectiveness of limiting formaldehyde emission from plywood

CONCLUSIONS

1. The use of acetoacetate groups in the form of the ethyl acetoacetate enables a significant reduction in the emission of formaldehyde from plywood because they are capable of bonding free formaldehyde to chemically resistant methylene bridges.
2. Effectiveness of AcAcEt in reducing of HCHO emission depends on its amount spread onto the veneers and the temperature of esterification process.
3. The greater the amount of the acetoacetyl groups the lower emission of HCHO was achieved, even by as much as 66% in the case of its maximum amount (15%).
4. Along with the increase of the temperature of the esterification process the emission of formaldehyde was increased. Most probably it is the result of partial decomposition of acetoacetate groups and their reaction with copolymers of wood, which in turn limits their ability to react with free formaldehyde.

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Streszczenie: *Acetylooctan etylu jako łapacz formaldehydu w żywicy UF stosowanej do wytwarzania sklejek.* W pracy zbadano możliwość zastosowania grup acetylooctowych w postaci acetylooctanu etylu do obniżenia emisji formaldehydu ze sklejek zaklejanych żywicą UF. Acetylooctan etylu nanoszono na forniry przed ich zaklejeniem żywicą i następnie poddawano je estryfikacji w różnych temperaturach. Przeprowadzone badania wykazały, że zastosowanie grup acetylooctowych w tej postaci umożliwia znaczne obniżenie emisji formaldehydu ze sklejek. W wyniku ich wzajemnej reakcji następuje związanie HCHO w postaci odpornych chemicznie mostków metylenowych. Wykazano, że wraz ze wzrostem ilości wprowadzanego AcAcEt zmniejsza się emisja HCHO z wytworzonych sklejek, nawet aż o 66%, w przypadku jego maksymalnej ilości, wynoszącej 15%. Ponadto w przypadku nanoszenia AcAcEt na forniry, przed ich zaklejeniem żywicą UF, istotną rolę odgrywa temperatura acetylooctowania. W miarę jej wzrostu, od 20 do 60°C, wzrasta bowiem emisja formaldehydu ze sklejek. Najprawdopodobniej jest to wynikiem częściowego rozkładu grup acetylooctowych oraz ich reakcji z kopolimerami drewna, co w efekcie ogranicza ich zdolność do reakcji z formaldehydem.

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