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ACTIVATION ENERGY OF CURING REACTION OF PHENOLIC RESIN IN THE PRESENCE OF SOME SELECTED SPECIES OF WOOD

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Effect of various species of wood on the curing reaction of phenolic resin were examined by mean of differential thermal analysis (DTA) to evaluate the activation energy (E_a) of this process. It was found that all wood species decrease E_a in comparision to E_a of unfilled resin. Based on the values of E_a the species of wood may be divided into three groups.

INTRODUCTION

Various species of wood are characterized by different bonding properties even when the same adhesives are used under the same conditions. It is well know that chemical constituents of the wood substrate and its micro- and macrostructure influence bondability of wood.

Mizumachi [13], and Mizumachi and Morita [14] maintain that "the activation energy of a curing reaction must be studied for as many adhesive-wood combinations as possible". They studied the effect of various Asian wood species on E_a of the curing reaction of urea and phenolic resins. Urea resin used in their experiments had E_a of 121 kJ/mole, whereas phenolic resin showed E_a of 75 kJ/mole. The addition of wood powder of the examined species resulted in E_a ranging from 109 - 264 kJ/mole and 58 - 109 kJ/mole for urea and phenolis resin, respectively. In our previous studies [24] we determined E_a for the urea resin and 12 species of European and tropical woods. We found that the resin itself had E_a of curing reaction of 93 kJ/mole, while after mixing it with wood powder its E_a ranged from 73 - 102 kJ/mole.

A decrease in the E_a value of the curing process shows that there is a positive effect of wood constituents on the course of adhesion and

quality of wood bonding. From the technological point of view, this should lead to changes in adhesion parameters, i.e. shortening of time or reduction of temperature. It is worth mentioning that some adhesives are particulary sensitive to the presence in wood of extractive substances which may inhibit the process of adhesive curing [1 - 2, 4, 10, 12, 15 - 17, 22].

In this study effects of various species of wood on the curing reaction of phenolic resin were examined by means of DTA to evaluate the E_a of the curing reaction.

EXPERIMENTAL

Properties of commercional nonmodified phenolic resin K-50 produced by Plywood and Wood Chemical Processing Plant, Bydgoszcz are shown in table 1. The resin was mixed with powdered (less than 120 μm) wood of $8 \pm 1\%$ water content. The following species of wood were used: alder

Table 1

Properties of phenolic resin K-50
Właściwości żywicy fenolowej K-50

Determination Oznaczenie	Values Wartości
Density, g/cm³ Gęstość, g/cm³	1.215
Dynamic viscosity, mPa·s Lepkość dynamiczna, mPa·s	1550
Free phenol content, % Zawartość wolnego fenolu, %	1.10
Free formaldehyde content, % Zawartość wolnego formaldehydu, %	0.40
Solid residue, % Sucha pozostałość, %	50.75
pH	11.20

(*Alnus glutinosa* G a e r t n.), ash (*Fraxinus excelsior* L.), beech (*Fagus silvatica* L.), birch (*Betula verrucosa* E h r h.), fir (*Abies alba* M i l l.), larch (*Larix decidua* M i l l.), lime (*Tilia cordata* M i l l.), longhi (*Chrysophyllum* spp.), mahogany (*Swietenia mahagoni* J a c q.), oak (*Quercus robur* L.), pine (*Pinus silvestris* L.), teak (*Tectona grandis* L.) and walnut (*Juglans regia* L.). Apart from the above mentioned wood species, we also examined a tannin extract from oak as well as two model compounds, namely gallic acid and d-catechin.

The resin (10 g) was thoroughly mixed with 10% (by weight) of individual species of wood or tannin powder. Then thin layers of mixtures were placed on glass slides which were kept at room temperature for 24

hrs to let the solvent evaporate prior to DTA measurement. The apparatus used was a Hungarian derivatograph type I. Paulik- F. Paulik MOM Co. Budapest. Minimum of four DTA runs were made for each sample with different heating rates from 3.0 to 18.5 deg/min. The weight of each sample was 200 mg. α-Al_2O_3 was used as the reference material. Acti-

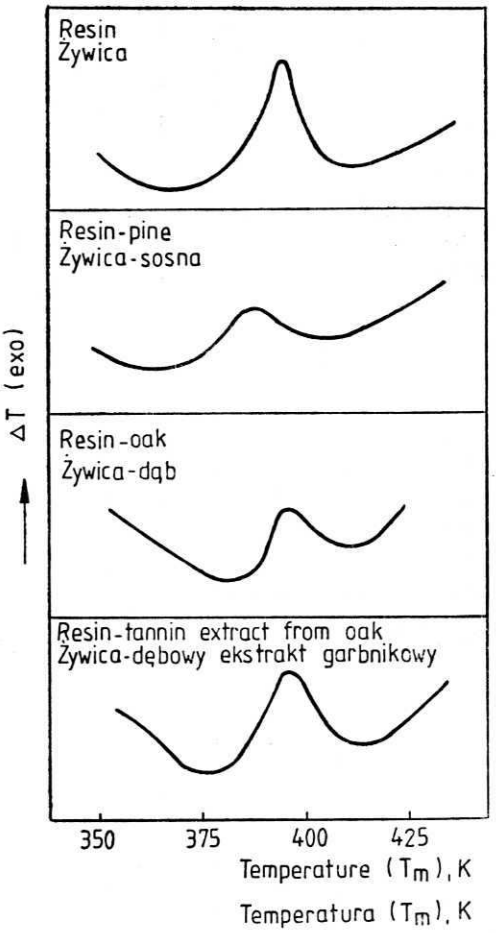

Fig. 1. DTA thermograms for curing reaction of K-50 phenolic resin and resin-wood and tannin systems (heating rate was 3.5±0.5 deg/min)

Rys. 1. Termogramy DTA reakcji sieciowania żywicy fenolowej K-50 i układów żywica-drewno oraz żywica-garbnik (szybkość ogrzewania 3,5±0,5 deg/min)

vation energy of the curing reaction of resin wood or tannin systems was calculated from DTA curves according to Kissinger [11]. The procedure proposed by him analyses the kinetics of chemical reactions from data of differential thermoanalytical curves using the following equation:

$$-\frac{E_a}{R} = \frac{d\ln(\Phi \cdot T_m^{-2})}{d(T_m^{-1})},$$

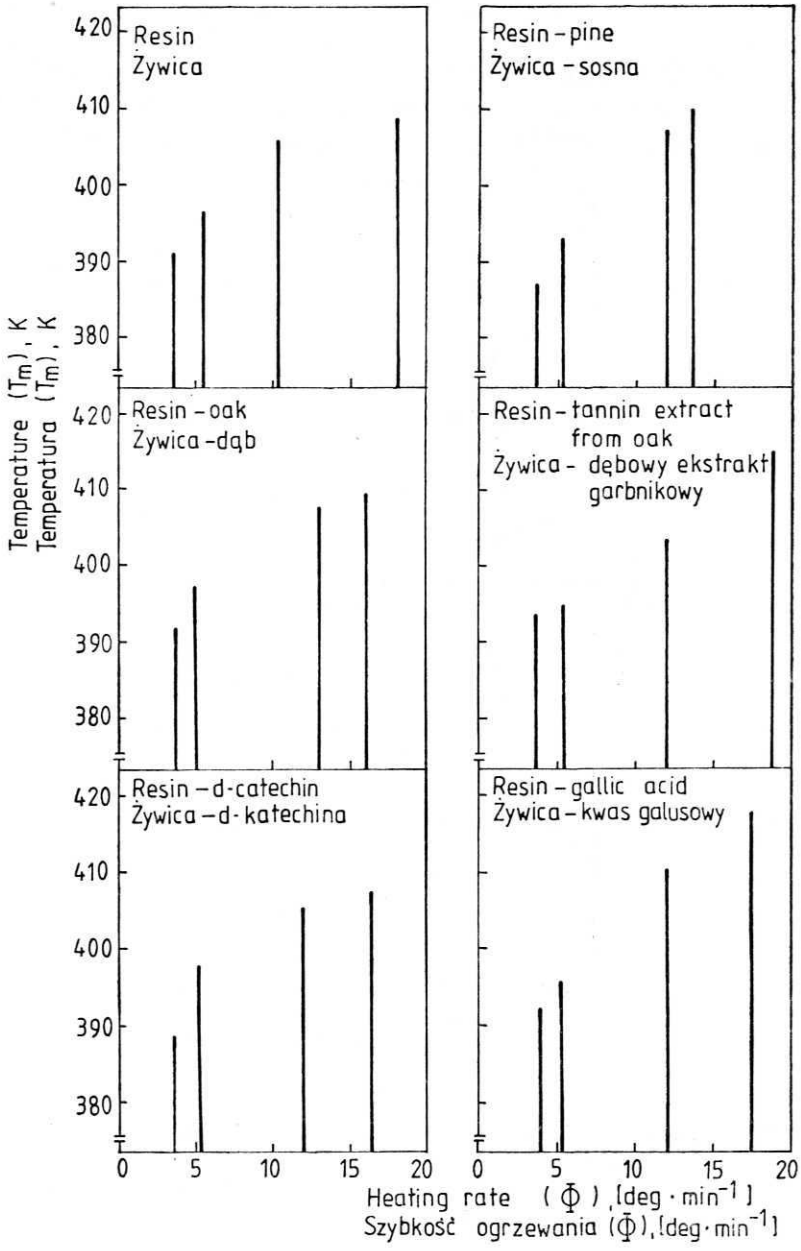

Fig. 2. Influence of the heating rate on the peak temperature displacement on DTA curve for curing reaction of K-50 phenolic resin and resin-wood and tannin systems

Rys. 2. Wpływ szybkości ogrzewania na przesunięcie pików temperatury na krzywej DTA dla reakcji sieciowania żywicy fenolowej K-50 i układów żywica-drewno oraz żywica-garbnik

where: T_m is the peak temperature (K) on DTA curve, Φ is the rate of heating (deg · s^{-1}), R is the gas constant and E_a is the activation energy of the reaction.

The E_a of the reaction can be obtained from the slope of the straight line in $\ln (\Phi \cdot T_m^{-2})$ vs T_m^{-1} plot (provided that peak temperatures are taken at several heating rates).

RESULTS AND DISCUSSION

Figure 1 presents typical DTA thermograms showing the course of the K-50 resin hardening process as well as the effect of different wood species and tannin on this process at a given heating rate. As we were

Table 2

Activation energy of the curing reaction of phenolic resin K-50 in presence of various species of wood
Energia aktywacji reakcji sieciowania żywicy fenolowej K-50 w obecności różnych gatunków drewna

Wood species Gatunki drewna	Activation energy kJ/mole Energia aktywacji kJ/mol
–	117.9
Mahogany Mahoń	56.3
Beech Buk	59.3
Longhi Longhia	61.1
Walnut Orzech	68.0
Lime Lipa	71.6
Ash Jesion	76.4
Pine Sosna	78.3
Teak Teak	83.5
Alder Olcha	89.4
Birch Brzoza	97.8
Fir Jodla	101.0
Larch Modrzew	101.2
Oak Dąb	112.2

only interested in the hardening process, the DTA run was stopped before temperature reached the level of thermal decomposition of the sample. It is quite clear from these thermograms that the endothermic region

occurs in the temperature of 360 - 430 K. This effect is caused by the evaporation of water and volatile low molecular weight compounds found in the resin. Within this area we notice an exothermic peak characteristic of a polycondensation reaction. It was found that this exothermic peak depends on the heating rate and is situated between 390 and 413 K. Figure 2 illustrates the influence of the heating rate on the peak temperature displacement on DTA curve for curing reaction of K-50 phenolic resin and resin-wood or tannin systems.

Table 2 lists calculated E_a values for K-50 resin and its combinations with the examined wood powders. It is evident from this data that all species of wood used in this experiment reduced E_a of the hardening process. It is practically impossible to explain differences in the obtained E_a values because wood even of the same bole is characterised by variations in chemical composition. The complexity of interactions between the phenolic resin and wood was discussed by Horioka and Gamo [9], and Abe et al. [3]. There is no agreement with regard to the role of wood constituents in the hardening process of phenolic adhesives. Many papers have been published indicating that individual both major and minor wood components may take an active part in the curing process.

It is maintained that cellulose, through its hydroxyl groups, exhibits high reactivity with phenolic resin. Experiments carried out by Chow [6] showed that E_a of the resin curing process was 46.9 kJ/mole while the same resin when mixed with cotton cellulose or cellobiose had E_a 32.7 and 24.2 kJ/mole respectively. Cherubim and Henn [5] emphasize that the reaction between phenolic resins and cellulose also depends on the pH of the resin. On the basis of IR and double refraction measurements Chow and Mukai [7] identified the presence of covalent bonds between the resin and cellulose. The same bonds were found between cellobiose and formaldehyde resins by Ramiah and Troughton [19] who applied thermoanalytical techniques. Also lignin may play an active role in the hardening of phenolic adhesives. In their studies on the mechanism of adhesion of phenolic resin to wood, Graham and Neogi [8] used ^{82}Br labelled 3,5-dibromo 4 hydroxybenzyl alcohol as a model of phenolic prepolymer. They concluded that phenolic resin-lignocellulose adhesion was not only limited to the van der Waals forces. The level of adhesion depended primarily on high energy covalent bonds occuring beetwen active groups present in the materials used in the experiment. It was also found that hydroxyl groups from phenylpropane units present in lignin react with the model compound according to second order reaction mechanism.

It is also believed that extractive substances of wood may play an active role in the hardening process as catalysts or inhibitors. Wood resins

and tannins are the most important among them. Seifert [23] found that resin from European coniferous trees containing polar resin acids show high affinity to polar adhesives, including phenolic resins. On the other hand, tannins are commonly considered to be inhibitors of this process [18, 20 - 21]. Results of our experiments do not confirm inhibiting effects of tannins on the curing process of the phenolic resin. Gallic acid and the tannin extract from oak cause a decrease of curing E_a of the examined resin to the level of 63.3 and 68.7 kJ/mole respectively. Comparatively insignificant differences in E_a values result from similarities of chemical properties of the gallic acid and ellagic acid whose derivatives are the main constituents of the oak tannin extract. On the other hand, a relatively small influence of d-catechin on E_a (110 kJ/mole) may be accounted for by a high rate of the condensation reaction which is competitive to the curing reaction.

CONCLUSIONS

1. Results obtained for E_a curing reaction of the examined commercial phenolic resin in the presence of the experimental 13 species of wood indicate that all these wood species decrease E_a in comparison to the E_a of the pure (unfilled) resin. Probably the presence of hydroxyl groups on surface of wood substance, which promoted the first stage of curing reaction with ether links formation caused this result.

2. According to the values of E_a obtained in our experiments the 13 species of wood may be divided into 3 groups:

— Wood species which reduce E_a of the curing reaction by 40 - - 60 kJ/mole. These species are: mahogany, beech, longhi, walnut, lime, ash and pine.

— Wood species which reduce E_a by 20 - 40 kJ/mole e.g. teak, alder and birch.

— Wood species for which E_a is similar to the E_a of the unfilled resin such as fir, larch and oak.

The values of E_a presented above could be additional criterion to estimation of phenolic resins technological hardening parameters.

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ENERGIA AKTYWACJI REAKCJI SIECIOWANIA ŻYWICY FENOLOWEJ W OBECNOŚCI WYBRANYCH GATUNKÓW DREWNA

Streszczenie

Celem pracy było poznanie wpływu wybranych gatunków drewna na wartość energii aktywacji (E_a) reakcji sieciowania termoutwardzalnych klejowych żywic fenolowych. Do doświadczeń użyto żywicy fenolowej K-50, 13 gatunków drewna oraz dębowego ekstraktu garbnikowego, d-katechiny i kwasu galusowego. Na podstawie danych uzyskanych z różnicowej analizy termicznej (DTA) obliczono E_a przy wykorzystaniu założeń opracowanych przez Kissingera.

W konkluzji stwierdzono, że E_a reakcji sieciowania żywicy K-50 wynosi 117,9 kJ/mol. Wszystkie uwzględnione w doświadczeniach gatunki drewna i substancje garbnikowe obniżały E_a reakcji sieciowania żywicy. Na podstawie wartości E_a można dokonać podziału poszczególnych gatunków drewna na następujące trzy grupy:

1. Gatunki, których obecność w żywicy powoduje znaczące, o 60 - 40 kJ/mol obniżenie E_a i którymi są: mahoń, buk, longhia, orzech, lipa, jesion i sosna. Ponadto do tej grupy można zaliczyć substancje garbnikowe.
2. Gatunki obniżające E_a o 40 - 20 kJ/mol, takie jak teak, olcha, brzoza.
3. Gatunki, dla których E_a jest porównywalna z wartością stwierdzoną dla żywicy K-50. Do gatunków tych zaliczono: jodłę, modrzew, dąb.