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The effect of organofunctional nanosilica on the cross-linking process and thermal resistance of UF resin

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Abstract The paper investigates the effect of surface modification of fumed nanosilica with (3-aminopropyl) triethoxysilane (APTES) on the kinetics and thermal stability of urea-formaldehyde (UF) resin. In the course of the investigation, nanoparticles were modified with APTES in the ratio 1, 2, 3, 4 and 5 part by weight (PBW) per 100 PBW of SiO_2. The parameters of curing kinetics of the resin, the conversion degree and its thermal stability were determined with use of differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). The effect of nanosilica silanization on the curing process of resin was evaluated by determining the gel time at 100 °C and the activation energy (E_a) of the cross-linking process, the initial and final temperature of the reaction (T_{onset}, T_{endset}), the maximum value of the exothermic peak (T_p), the amount of emitted heat (ΔH_{Tp}) and the conversion degree (α_{Tp}) that responds to T_p. With the maximum level of silica modification, we have noted a decrease in the reactivity of the resin, which is manifested by a slightly longer gel time of the resin as well as an increase in the value of activation energy of the cross-linking process. It is accompanied by a slight decrease of resin conversion degree α_{Tp}. The modification of silica, regardless of the amount of silane inoculated on its surface, results in the increase in the thermal stability of UF resin.

Introduction

As an interdisciplinary science, nanotechnology has been applied to investigations on the manufacturing and surface finishing of wood-based materials. According to the studies conducted so far, nanoparticles introduced to the adhesive significantly affect its properties such as viscosity, strength, water resistance, thermal resistance and other barrier properties. In case of lacquers the addition of nanoparticles increases the resistance to scratching, UV radiation and fire. The most universal nanoscopic additive is synthetic silica commonly used in the pharmacy, cosmetics, construction chemicals, lacquers and others. The paper by Dukarska and Czarnecki shows that small addition of nano-SiO_2 to MUPF resin makes it possible to optimize the process of plywood production by reducing the amount of resin mixture in the process of gluing the sheets of veneer [1]. According to Leonovich et al., Lin et al., Shi et al., Roumeli et al. the introduction of nanosilica into urea-formaldehyde resin contributes to the growth of physico-mechanical properties of particleboards, MDF and wood [2–5]. Small amount of nano-SiO_2 added to UF resin improves the strength parameters of boards produced from rape straw particles [6, 7]. However, to effectively strengthen the polymer, nanoparticles must be homogeneously dispersed in it [8]. That is why, nanoparticles are modified on the surface and, therefore, their adhesive properties are improved and chemical affinity to polymer is increased. Moreover, it is possible to partially or even completely change the surface properties from hydrophilic to hydrophobic ones. In case of nano-SiO_2, the efficiency of surface modification depends on the type and amount of the applied modifier, pH in the

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environment, the duration and method of modification and the applied catalyzing additives [9, 10]. The major criterion for the choice of proadhesive agent is the ability of its organofunctional group to create a chemical bond with a polymer. The most widely used modifiers of nanosilica surface are silane coupling agents: alkoxy-, chloro-, epoxy- and methacryloxy-functional with the general chemical formula $(OR)_3$-SiO-X, where X means a functional group, e.g. amine group, bounded to a Si atom with an alkyl chain; OR means most frequently an alkoxy group which can be easily subjected to hydrolysis and shows chemical affinity to both the filler and polymer [11, 12]. Owing to alkoxy groups, these compounds can be easily coupled with any material that has hydroxyl groups on the surface. The modifier selection depends on its functional groups able to interact with the surface of silica as well as with the polymer. In case of urea-formaldehyde and phenol-formaldehyde resins, the most commonly used proadhesive agents are aminosilanes. The literature on the subject shows that organofunctional silanes do not demonstrate greater reactivity to silanol groups present on the silica surface; however, the reaction is catalyzed by the presence of amine. Blitz et al. showed that the basic amines interact with acidic silanol proton and therefore they increase nucleophilicity of the surface oxygen, thus increasing its reactivity [13, 14]. Hence, organofunctional silanes including amine groups are highly reactive to silanols on the surface of silica although they do not autocatalyze their own reaction [15, 16].

The most efficient modification degree is attained when only a little amount of proadhesive agents is used, i.e. 1–5 PBW per 100 PBW of silica. Larger amounts of these agents do not bring such significant changes in the surface properties of nanofillers [17]. If there is a need to increase the chemical interaction of nanofiller to the polymer matrix, it is necessary to apply silicas with higher degree of surface modification, i.e. 5, 10 and 20 PBW per 100 PBW of SiO_2 [18]. Silicas modified on the surface with proadhesive agents or compounds containing reactive groups -NH, −COOH and others are also used as precursors in the process of manufacturing more complex hybrid materials. An example here is nanosilica modified in the initial phase with aminosilane, and later with e.g. biopolymers such as proteins [19], lignin [20] or cellulose [21]. Results of the research on obtaining di- and multifunctional nanosilica also seem interesting. In the course of the process, silica is subjected to two-stage surface modification: first with use of one kind of organosilane and next with silane of a different kind, different properties [16].

So far, in the investigations on the use of nanosilica as an additive to urea-formaldehyde resin applied in production of plywood, particleboards and OSB, researchers used mainly non-modified silicas [1, 5, 22]. Roumeli et al. show that silica non-modified with proadhesive agents, when introduced into UF resin, tends to create aggregates of various size and their number increases along with the silica content [5]. This phenomenon may unfavourably affect the process of resin condensation and the strength of adhesive bonds. Uniform distribution of nanoparticles in the resin solution will lead to the maximum strengthening effect and homogeneity of properties for both the resin and wood-based materials produced with its use. Taking into account the fact that the curing process of UF resin and its adhesive properties greatly depend on the conditions in which the reaction takes place, the authors undertook investigations whose aim was to determine the optimum quantity of aminosilane used for modifying the surface of fumed nanosilica added to UF resin. Our research attempts also to explain how the degree of surface modification of silica with the selected aminosilane affect the kinetics of cross-linking process and thermal stability of nanocomposite UF resin/nano-SiO_2.

Experimental

Materials

In the course of the investigations, we used urea-formaldehyde UF resin (Poland, Silekol, Kędzierzyn Koźle) applied in the production of plywood, with viscosity according to No 4 Ford – 93 s, density at 20 °C 1.285 g cm^{-3}, solids content 65 %, pH 8.7, gel time at 100 °C 150 s and miscibility with water 1.5 cm^3 g^{-1}. Into the resin we introduced fumed silica Orisil 200 (produce of Ukraine, Orisil Kalusb, Subsidiary of Orisil). The surface modification was conducted with use of silane coupling agent, i.e. (3-aminopropyl) triethoxysilane (APTES, brand U-13 produced by Unisil, Poland). It is used mainly as an adhesion promoter and surface modifier of non organic fillers for numerous polymer systems, including phenol-, melamine- and urea-formaldehyde resins. Basic physicomechanical properties of silica and aminosilane are presented in Table 1.

Surface modification of nano-SiO_2

Silica modification was performed at room temperature using so called "dry" method described by Krysztafkiewicz et al. and Klapiszewski et al. [10, 23]. The process involved applying 1, 2, 3, 4 and 5 part by weight (PBW) APTES per 100 PBW of SiO_2 on the silica surface. Prior to silica modification, APTES was hydrolized in methanol and water solvent (4:1 *w*/w). Then, the hydrolized silane was sprayed directly on the silica surface. After each application of the modifying solution, intense stirring was applied with a mechanical stirrer and constant speed of 1200 RPM/min. When the entire modifying solution was used, the stirring continued for 1 h. Next, the modified silica was first dried in a vacuum evaporator to evaporate the solvent (methanol), and then in an oven at 105 °C for 2 h.

Table 1 Typical properties of Orisil 200 and APTES

Orisil 200		APTES	
Property	Value	Property	Value
Specific surface area BET, $m^2 g^{-1}$	200 ± 25	Molecular weight, $g\ mol^{-1}$	221.4
pH value in 4 % aqueous dispersion	3.6–4.3	Density, $g\ cm^{-3}$	0.951
Tamped density, $g\ l^{-1}$	50	Refractive index	1.42
SiO_2 content, %, min	99.9	Viscosity, 25 °C	1.6
Fe_2O_3 content %, max.	0.05	Boiling point, °C mm Hg^{-1}	122–123/30
TiO_2 content, %, max.	0.03		

As in the process of UF resin condensation certain amount of water is released, we also determined water absorption capacity of silica before and after the modification. The study involved gradual dispensing of distilled water from a burette to a flask containing the tested silica sample (10 g ± 0.01 g). The endpoint of the measurement was the point at which the excess of a single drop of water resulted in clear fluidization of the aqueous suspension of colloidal silica [24]. Water absorption capacity of silica was determined as the ratio of the total volume of absorbed water to the initial weight of silica expressed in cm^3 of water per 100 g of silica. The final result was the average of five individual measurements for each investigated variants.

Preparation of UF resin/nano-SiO₂ nanocomposite

The adhesive mixtures were prepared by supplementing the resin solution with non-modified or modified silica in the amount of 2 PBW of nano-SiO₂ per 100 PBW of UF resin. After adding the nanofiller, the solution was first stirred with a mechanical stirrer and then homogenized using CAT-500 device to achieve appropriate homogenization degree and dispersion of the nanofiller particles in the resin solution. A sample containing 100 g of the mixture was homogenized for 2 min at 11,000 RPM/min.

Characterization

The effect of silanization of fumed silica nanoparticles on the reactivity of adhesive mixtures made from UF resin and nano-SiO₂ was determined based on the gel time at 100 °C and the value of activation energy of the cross-linking process. Gel time of the investigated adhesive mixtures at 100 °C was determined based on the Polish standard PN-C89352–3 [25]. The method consists in measuring the time since initiation of the curing reaction until the final gel point, i.e. complete curing of the resin sample. The samples of individual adhesive resins (10 ± 0.1 g) were placed in test tubes that were then heated in a water bath to 100 °C. The gel time was assumed as the time from placing the sample at 100 °C until it was completely cured. The presented results are the average of five

individual measurements. The value of activation energy (E_a) was determined using DSC analysis and Kissinger [26] and Ozawa [27] methods, which are commonly used to characterize the polycondensation process of resins [28–30]. Activation energy is determined on the basis of Arrhenius equation:

$$k = Ae^{\left(\frac{-E_a}{RT}\right)} \tag{1}$$

where: k – rate constant, A – pre-exponential factor, E_a – activation energy (kJ mol^{-1}), R – gas constant (kJ mol^{-1} K^{-1}), T – absolute temperature (K). The DSC analysis interprets the eq. as:

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E_a}{RT}\right)\cdot(1-\alpha)^n \tag{2}$$

where α is the conversion degree determined on the basis of enthalpy of cross-linking reaction in the time t and the enthalpy of the cross-linking process termination (ΔH_{total}) determined from DSC thermograms.

$$\alpha = \frac{\Delta H_t}{\Delta H_{total}} \tag{3}$$

This equation was also used to determine the effect of nanosilica silanization on the conversion degree of the adhesive mixture (α_{T_p}) achieved for the extreme temperature peak T_p. The value of this parameter was estimated as the ratio of the heat emitted at the extreme temperature peak T_p (ΔH_{T_p}) to total enthalpy of the curing process (ΔH_{total}).

Therefore, the dependence [1] can be shown as the equation

$$\ln k = \ln\left[\frac{\left(\frac{d\alpha}{dt}\right)}{(1-\alpha)^n}\right] = \ln A - \frac{E_a}{RT} \tag{4}$$

According to Kissinger method:

$$E_a \beta\left(RT_p^2\right) = Ae^{\frac{-E_a}{RT_p}} \tag{5}$$

where β is the heating rate defined according to the dependence: $\beta = dT/dt$.

DSC analysis was made in closed aluminium crucibles using Setaram company LABSYS TM thermobalance; we applied four heating rates: 3, 5, 10 and 20 °C min^{-1} in the temperature range 20–200 °C and helium flow of 2 dm^3 h^{-1}. Based on this analysis, we also determined the initial and final temperature of the curing reaction in the investigated nanocomposite resins (T_{onset}, T_{endset}), the maximum value of the exothermic peak (T_p) as well as the amount of heat (ΔH_{Tp}) and the conversion degree (α_{Tp}) relevant to T_p. The presented results are average from three analyses per each variant.

In order to determine the influence of nanosilica modification on the thermal stability of UF resin, we used the thermogravimetric analysis (TG-DTG) to measure the change of mass of a sample heated in polythermal conditions. The analysis was made in open platinum crucibles with helium flow of 2 dm^3 h^{-1} and heating rate of 10 °C min^{-1} within the range of 20–650 °C.

Results and discussion

Taking into the account the fact that fillers used in the production of plywood are characterized by considerable hygroscopicity and capacity to absorb water (including condensed water), in our investigations we also determined the effect of the amount of applied APTES on the water absorption capacity of silica. Results of these tests are presented in Table 2: the data show that along with the growth of modification level, the hydrophobicity degree of silica surface increases. The greatest changes were observed for over 3 PBW of APTES per 100 PBW of nano-SiO$_2$. The application of silane in the amount of 1–3 PBW results in a gradual degree of water absorption capacity by 10 % in relation to the non-modified silica. Further growth in the amount of APTES up to 5 PBW reduced water absorption capacity by 38 %. From these findings we can infer that the amount of APTES applied on the surface of silica should not exceed 3 PBW/100 PBW of SiO$_2$. Higher hydrophobicity of nanoparticles would deteriorate the hygroscopicity of water released as a by-product of the condensation of UF resin, which can also disrupt the course of the process.

Table 2 Absorption capacity of nano-SiO$_2$ before and after the modification with APTES

PBW APTES/100 PBW SiO$_2$	Water absorption capacity [cm^3 H$_2$O/ 100 g nano-SiO$_2$]	Standard deviation
0	1060	12.5
1	1000	18.6
2	960	15.7
3	870	2.3
4	720	8.5
5	650	19.9

On the surface of silica there are highly reactive silanol groups which can form hydrogen bonds or participate in condensation reactions in resins [5]. Dukarska and Czarnecki prove that introducing fumed silica into MUPF resin, in the amount of 2 PBW/100 PBW of the adhesive reduces the value of activation energy of the cross-linking process [1]. Table 3 shows the effect of non-modified nano-SiO$_2$ on the reactivity of urea resin determined on the basis of activation energy measured with use of Kissinger and Ozawa methods. Data presented in the table are correlated with the previous findings. The addition of 2 PBW of silica non-modified on the surface into 100 PBW of UF resin results in a slight decrease in the value of activation energy. Similar results were described in the paper by Park and Jeong, which investigates the influence of adding nanoclay as a filler in melamine-formaldehyde resin [31]. The researchers found out that the introduction of nanoclay in the amount of 1–3 % reduced the value of activation energy of the investigated resin. Increasing the amount of nanoclay up to 5 % has a deactivating effect demonstrated by the higher value of activation energy. The investigations by Roumeli et al. also confirm the proposition about the deactivating effect of larger quantities of nanosilica on the kinetics of cross-linking process [5]. The preliminary studies, which we conducted, also prove that adding up to 2 % (w/w) of nanosilica to UF resin leads to a slight decrease of the activation energy. The deactivating effect of nano-SiO$_2$ is observed when the amount of silica added to the resin is higher. It probably results from the fact that nanoparticles of SiO$_2$ interact with a polymer chain by forming hydrogen bonds or participating in the reaction of condensation. Moreover, nanoparticles of SiO$_2$ constitute a physical barrier which disrupts the continuity of polymer matrix and inhibits reactions between the reactive groups of urea and formaldehyde.

As mentioned in the introduction, polymer systems can be efficiently strengthened with nanofillers only if the fillers are homogeneously dispersed in polymers. That is why, nanosilica used in the investigation was subjected to surface modification. Below we present results of investigations on the kinetics of the cross-linking process of UF resin with the addition of fumed silica nanoparticles, whose surface was treated with various amounts of APTES. The studies were made with use of DSC analysis. On its basis we determined the gel time at 100 °C and the activation energy of the cross-linking process of UF resin depending on the modification degree of nanosilica added to the resin, the initial and final temperature of the cross-linking process (T_{onset}, T_{endset}), the maximum of the exothermic temperature peak (T_p), the amount of heat ΔH_{Tp} responding to T_p. The results of this analysis are shown in Table 3 and Fig. 1. The analysis of the attained results shows that the modification of nanosilica with aminosilane in the amount of 5 PBW per 100 PBW of SiO$_2$, results in a slightly longer gel time of the investigated adhesives. With the maximum level of modification, the gel time was lengthened by approx. 10 % in relation to both pure

Table 3 The effect of APTES modification of nano-SiO$_2$ on the kinetic parameters of polycondensation process of UF resin

PBW APTES/100 PBW SiO$_2$	Gel times	E$_a$ J mol^{-1}		T$_{onset}$ °C	T$_p$ °C	T$_{endset}$ °C	ΔH$_{Tp}$ J g^{-1}	α$_{Tp}$ %
		Kissinger	Ozawa					
UF resin (pure)	150	93.19[*]	94.45[*]	89.02	95.14	100.56	55.71	62.9
0	149	89.68	90.77	87.26	92.83	97.43	35.80	57.6
1	150	91.47	92.76	87.02	91.32	97.97	33.61	54.2
2	155	92.32	94.02	87.43	92.45	97.67	31.49	54.7
3	159	92.45	93.88	88.20	93.94	99.05	30.17	55.0
4	161	92.24	93.85	88.58	95.03	99.69	29.97	54.3
5	163	93.98	94.78	89.37	95.65	99.52	30.41	53.1

Values of T$_{onset}$, T$_p$, T$_{endset}$, ΔH$_{Tp}$ and α$_{Tp}$ determined at heat rate 10°C min^{-1}

[*] correlation coefficients for all the studied variants are in the range of 0.98–1.0

resin and the resin with addition of non-modified silica (the gel time varied in the range of 150 to 163 s). It indicates only minor decrease in the reactivity of the adhesive mixture. This results are consistent with the conclusion reached by Han et al. [32] and with the kinetic parameters determined based on DSC analysis.

The curing process of UF resin is an exothermic reaction and therefore, an assumption is made that enthalpy is proportional to the degree of conversion α in the cross-linking process [33]. The conversion degree is defined as the ratio of the amount of heat released in time to the total heat of reaction [34]. Having accepted these assumptions, we estimated the conversion degree α$_{Tp}$ of UF resin which responds to the maximum rate of the condensation reaction (according to equation 3) depending on the modification degree of nanosilica added to the resin (Table 3).

From the analysis of activation energy of investigated mixed adhesives we can infer that functionalization of nanosilica in the amount of 1–5 PBW of APTES does not significantly affect the reactivity of UF resin determined by the values of activation energy. It was observed that increasing of amount of APTES

inoculated on surface of silica causes slight increase of activation energy. At maximum amount of APTES the value of E$_a$ increased by 13 %. The attained result is comparable to the value determined for the pure UF resin, but higher than for resin with addition of non-modified nanosilica. Similar trends are observed for the values of temperatures characteristic of initial, final and central periods of the cross-linking process (T$_{onset}$, T$_p$ and T$_{endset}$). The values prove that, in relation to non-modified silica, the addition of nanosilica modified with no more than 2 PBW of APTES does not affect the curing process of the resin. When the amount of APTES is increased up to 5 PBW/100 PBW of nanosilica, the values of T$_{onset}$, T$_p$ and T$_{endset}$ increase to the level characteristic of pure UF resin. Data presented in Table 3 prove that the increase in modification degree of silica surface leads to the decrease in the enthalpy of curing process. Addition of non-modified silica to UF resin leads to significant decrease heat flow by 35 %. Inoculating aminosilane on the surface of nanosilica in the amount of 5 PBW/100 PBW of SiO$_2$ causes further decrease of ΔH$_{Tp}$ from 35.8 to 30.41 J g^{-1}, i.e. by 8 %. The reduction of the amount of heat released in the condensation process is accompanied by a decrease of the conversion degree relevant to T$_p$. Introduction of non-modified nanosilica into the UF resin reduces the value of conversion degree by 8.5 %. Silanization of the nano-SiO$_2$ surface leads to further reduction of this parameter. For the maximum amount of APTES it was observed decrease of conversion degree by 6 %, in comparison to adhesive mixture containing non-modified silica.

The interpretation of the obtained results should take into account the fact that the curing of UF resin is a complex process, which depends on numerous factors, such as pH, viscosity, concentration of reactive groups. The investigations show that the introduction of nanosilica into the resin changes the kinetics of the curing process. Moreover, inoculating aminosilane on the surface of silica brings in additional factors, which disrupt the course of the process. At the beginning of cross-linking process, particles of pure UF resin have low molecular mass and they easily diffuse and react with one
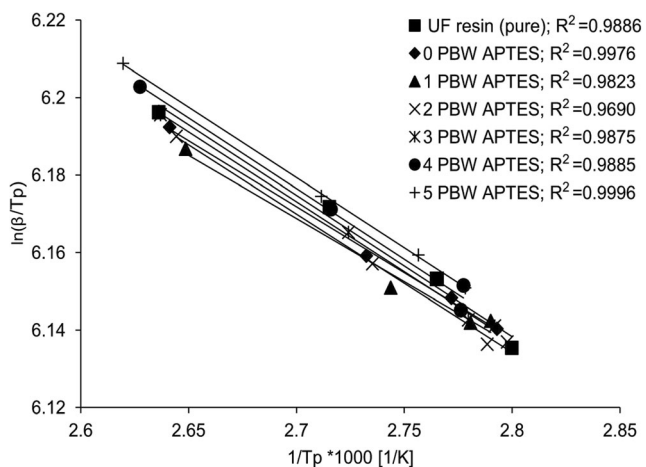

Fig. 1 Kissinger's plot for studied samples in depending on the amount of APTES/100 PBW of nano-SiO$_2$

another. As the reaction progresses, the concentration of reactive functional groups becomes smaller, which is accompanied by the release of condensed water [35]. The presence of water contributes to the decrease in the concentration of reacting substances and slows down the process at the early stage of resin condensation. Therefore, we can infer that the addition of hydrophilic nanosilica to UF resin causes, at the initial stage, the absorption of water and acceleration of the curing process, which is manifested by the decrease in temperatures T_{onset}, T_p and T_{ensed}. Another consequence is the reduction of activation energy. Silanization of the nanostructure surface enhances the hydrophobic character of the silica surface and that leads to lower absorption capacity (Table 1) of water both included in the resin and released in the course of condensation. As a result, the cross-linking process is inhibited, which is demonstrated by the higher values of T_{onset}, T_p and T_{endset}. The increased hydrophobicity of nanosilica surface unfavourably affects the conversion degree of the resin, especially at the initial stage of its condensation. The delay of the cross-linking reaction results also from the fact that both modified and non-modified nanosilica introduced into the resin is a physical barrier to the heat flow. Since silica has much larger heat capacity than pure UF resin, its addition leads to the increase of heat capacity of the resin. As a result, the amount of heat ΔH_{Tp} released in the course of resin condensation is considerably reduced. There are a lot of research works on the effect of type, size, dispersion degree and concentration of nanoparticles on the heat capacity of various nanomaterials [36–40]. They all show that nanostructures formed in various materials are responsible for the growth in their heat capacity [38]. Researchers also found out that nanocomposites with a high degree of nanoparticles dispersion were characterized by much larger heat capacity than systems containing their agglomerates [40, 41]. It can be explained by the relation between the value of enthalpy ΔH_{Tp} and the degree of silanization of silica. The gradual increase in the modification degree of silica, as well as using high sheer stress in the homogenization process of mixed adhesive, resulted in the continuing improvement of the adhesive homogeneity, high level of nanoparticles dispersion and growth of their specific surface area. Consequently, the number of nanosilica agglomerates decreased and the heat capacity of the investigated adhesives became larger. As a result, we recorded a decrease in the amount of heat released in the curing process of the resin.

Along with the reduction in the amount of released heat ΔH_{Tp} we recorded a decrease in the conversion degree in the curing process. It results from the fact that nanoparticles of silica constitute a steric hindrance, which restricts the motion of polymer chain of the resin. The surface modification of silica nanoparticles leads to the fragmentation of their agglomerates, which results in the increase in their specific surface area in relation to the volume of nanoparticles introduced to the resin. Therefore, joining shorter or longer polymer chains becomes more difficult and the cross-linking level of the resin decreases. The process is made even more difficult by the presence of amine groups inoculated on the surface of silica. According to Jesionowski and Krysztafkiewicz they take part in the formation of hydrogen bonds between the neighbouring particles of modified silica [42].

The obtained values of gel time, activation energy and the temperatures characteristic for the resin curing (as compared with the resin supplemented with non-modified silica) indicated only insignificant effect of silica modification with aminosilane in the amount of 5 PBW per 100 PBW of SiO_2 on the cross-linking process of UF resin. This fact is important when this type of hybrid resin is used in the manufacture of wood-based materials such as plywood or particleboard, as the reactivity of the adhesive resin determines the conditions of pressing, i.e. its time and temperature. Moreover, insufficient dispersion of nano-SiO_2, and the presence of nanoparticles aggregates and agglomerates in the adhesive resin solution may weaken the adhesive joints and thereby result in spontaneous fractures that would reduce the strength of the wood-based materials. Another issue is related to technical difficulties that may occur when using this type of resin is used for gluing wood chips. Too low a degree of nanoparticle dispersion and their aggregates in the adhesive resin solution may obstruct the adhesive spraying through the injection nozzles (nozzle clogging) and achieving a uniform cover on the chip surface. Therefore, the criterion more important in determining the degree of nanosilica modification used as an additive to UF adhesive resin in the production of wood-based materials is an adequate degree of nanoparticle dispersion and not the effect of modification with aminosilane on the cross-linking process.

In order to fully evaluate the effect of surface modification of nanosilica with APTES on thermal properties of UF resin, we investigated the course of thermal decomposition of the investigated adhesives. Our studies are illustrated by thermogravimetric curves TG and DTG: they characterize the changes in masses in the temperature range 20–650 °C (Fig. 2). The course of TG thermographs of UF resin with the addition of nanosilica modified at various degrees was correlated with the curve of the resin with the addition of non-modified silica. Studies made by Roumeli et al. show that introducing nano-SiO_2 into the resin causes the growth in heat resistance of the resin, which results from the fact that silica itself is thermally stable up to 500 °C [5]. The obtained results prove that the thermal degradation of UF resin with the addition of silica with various degree of silanization proceeds in a comparable way and the thermogravimetric curves have a similar profile. In the presented thermograms of investigated mixed adhesives we can distinguish three stages of thermal decomposition. The first one in the temperature range from 30 to 105 °C, with the maximum endothermic peak at 89 °C and mass decrement at
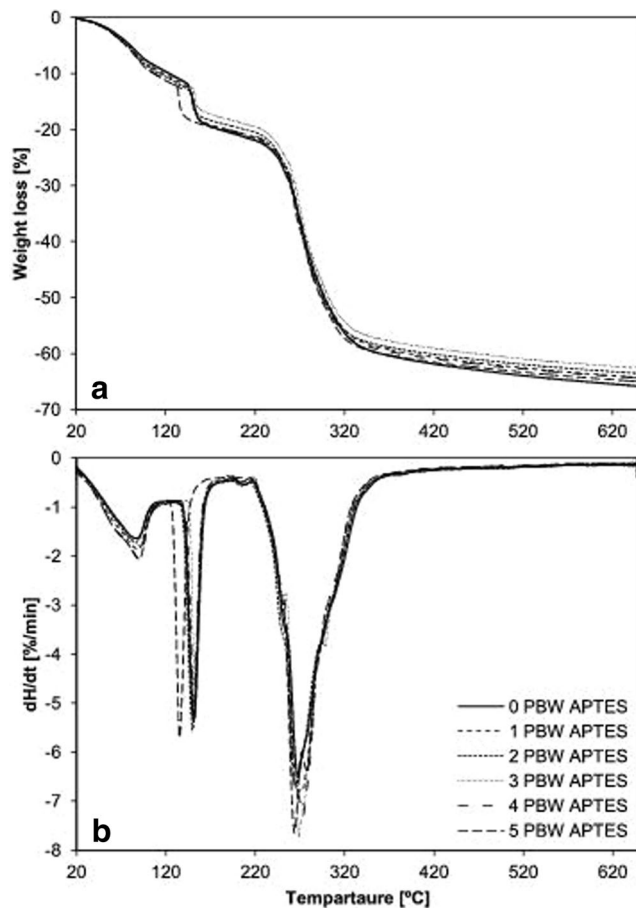
Fig. 2 Thermal stability of UF resin with the addition of nanosilica modified with various amounts of APTES/100 PBW of nano-SiO_2 (10 °C min^{-1}): **a** – TG, **b** – DTG

6 ± 0.5 %, corresponds to the reaction of resin condensation; yet the peaks within 135–153 °C are ascribed to water release. A small shift of peak maximum toward lower temperatures for adhesive mixtures containing modified silica results from the fact the dispersion of particles in the resin solution is higher than in case of non-modified silica and, therefore, volatile products can be more easily released. Moreover, what also matters here is the hydrophobic character of nano-SiO_2 surface. Modification with aminosilane changes its property into even more hydrophobic and that restrains the amount of absorbed water. The literature on the subject shows that the greatest decomposition of the resin takes place in temperature above 200 °C. In Fig. 2b we recorded peaks with maximum at 265 ± 2 °C regardless of the modification degree of nanosilica. In this temperature the degradation of ethylene bridges also occurs [43, 44]. Correspondingly, we observe 30 % mass decrement and the occurring 1–2 % differences are within margin of error. The total mass decrement of investigated mixed adhesives which were recorded at the maximum measurement temperature, i.e. 650 °C, is within 62–66 %. The highest thermal stability was observed for adhesives with the addition of modified silica. The increase of thermal stability of adhesive

mixtures containing the modified silica results from the better dispersion of nanoparticles in the resin solution and, therefore, the improvement of boundary values. In case of the maximum amount of aminosilane used in the investigations, the growth in thermal stability may results from the presence of silica nanostructures. However, it may also prove the presence of hydrogen bonds between polymer chains of UF resin and nanoparticles of silica, which are responsible for higher thermal stability of the investigated nanocomposite UF resin.

Conclusion

The investigations on the kinetics and conversion degree of the cross-linking reaction of UF resin with addition of silica modified with nanosilane show that the modifying agent does not significantly affect the course of reaction. We have found out that the surface modification of nano-SiO_2 leads to slight reduction of the cross-linking reaction rate and decreases the conversion degree of the resin when silane is applied in the amount of 5 PBW per 100 PBW of SiO_2. With such an amount of silane, the condensation process of the resin occurs when the activation energy is higher and gel time is longer than in case of UF resin with addition of non-modified silica. The silanization of silica leads also to a slight decrease in the conversion degree of the resin in relation to resin as well as resin with addition of non-modified silica. Nevertheless, the thermogravimetric tests prove that the thermal stability of the resin grows along with the increase in the modification degree of nanoparticles of fumed silica, which is probably related with better dispersion of nanoparticles in the resin solution and the presence of hydrogen bonds between polymer chains of UF resin and nanoparticles of silica.

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