



Synthesis, characterization and thermal analysis of urea–formaldehyde/nanoSiO₂ resins

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ABSTRACT

In the present work urea–formaldehyde resins (UF) containing different amounts of SiO₂ nanoparticles were synthesized and studied in depth. All the hybrids were characterized with Fourier transform infrared spectroscopy (FTIR) and powder X-ray diffractometry (XRD), while the dispersion of nanoparticles was studied with scanning electron microscopy with associated energy dispersive X-ray spectrometer (SEM/EDS). It was found that even though silanol groups of SiO₂ can interact with UF resin and form hydrogen bonds, aggregates of SiO₂ nanoparticles can still be formed in UF resin. Their size increases as SiO₂ content is increased. The curing reactions were examined with differential scanning calorimetry (DSC) and it was revealed that curing temperature of UF resin is slightly affected by the addition of nanoparticles. Furthermore, the activation energy of the curing reactions, for every hybrid, was calculated using the Kissinger's method, which implied the existence of interactions between the nanoparticles and the polymer chain. Thermogravimetric analysis (TGA) revealed that SiO₂ nanoparticles do not have an effect in the thermal stability of the resin. From the application of the prepared UF/SiO₂ resins in wood panels it was found that the mechanical properties of the panels, like the internal bond and the modulus of rupture, are enhanced with increasing nanoSiO₂ concentration.

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1. Introduction

Urea–formaldehyde resins have been extensively used by the wood-based panel industry for more than 100 years, due to their good performance in the production of wood-based panels, as they have high reactivity and low cost. Their drawbacks are low water resistance and formaldehyde emission from the wood boards, resulting from the low stability of the amino–methylene bond. To overcome this problem, many attempts have been made, like modifying the resin synthesis methods and applying various types of hardeners or additives, etc. [1–3]. The main goal of the modern adhesive industry is to compromise these needs and produce effective UF resins with very low, if not zero, formaldehyde emissions. Furthermore, a drastic reduction in the formaldehyde emission with a significant improvement in the durability–stability of UF bonded wood products could extend the applications and markets for these products. One rather effective approach in order to reduce formaldehyde emission is to lower F/U molar ratio of the

synthesized resin [4–6]. However, this leads to a reduced crosslinking and thus, inferior performance of the resin, regarding to its mechanical strength and water resistance [4]. In addition to lowering the F/U molar ratio, a number of studies have focused on modifying the synthesis parameters of UF resins by manipulating parameters such as reaction pH [7–9], introduction of second urea addition [10] and the use of additives [11,12].

Additives in general, have modifying effects on the properties of the UF resins [13]. The most effective and common methods that have been used so far include the addition of small quantities of melamine in the case of more demanding applications. The use of other additives, like formaldehyde catchers has also been tested [14]. Also, the addition of trimethoxymethylmelamine and dimethoxymethylmelamine as cross-linking agents were found to be beneficial for durability [15]. Nowadays, technology offers the possibility of using additives with dimensions in the nano scale. Such materials seem promising because nanoparticles have large surface areas and can bring on new properties or even modify important properties of the resins that they are induced to, like reactivity. Especially the addition of nanoSiO₂ in UF resins, has been reported to enhance the mechanical properties of the resin [16–18] and therefore, needs to be studied in depth.

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In this work, the structure and performance of resin hybrids prepared by the mixing of a UF resin with SiO₂ nanoparticles at various ratios, were examined. Even though some authors investigated the properties of UF resins prepared under different reaction conditions, or even modified mixtures with different fillers, studies on thermal behavior of UF hybrids have been limited. Therefore, this study was conducted in order to investigate the influence of SiO₂ nanoparticles on the thermal behavior of UF resins, using DSC and TGA. Also, a thorough characterization of the new hybrids was performed using FTIR, SEM/EDS and XRD.

2. Experimental

2.1. Materials

The UF resins were supplied by Chimar Hellas and their synthesis will be discussed in the following.

Fumed SiO₂ nanoparticles (nanoSiO₂) used for hybrids preparation, were supplied by Degussa AG (Hanau, Germany) under the trade name AEROSIL® 200, having a specific surface area 200 m²/g, SiO₂ content >99.8% and average primary particle size 12 nm. All the other materials and solvents used for analytical methods were of analytical grade.

2.2. UF resin/nanoSiO₂ hybrids synthesis

The urea–formaldehyde (UF) resins prepared by Chimar Hellas, had final mole ratio F:U = 1.07 and resulted from the reaction of urea (U) with formaldehyde (F), following a two-step process as described in a previous paper [19]. Fumed SiO₂ nanoparticles were added in the UF resin at the levels of 1, 2, 3 and 3.5% (w/w). The UF/SiO₂ nanoparticles mixtures were mechanically stirred for 5 min before use. The pure UF resin sample was given the name UF-0 while the mixtures were named UF-1, UF-2, UF-3 and UF-4 respectively.

2.3. FTIR spectroscopy

The hybrids were studied with FTIR in two different polymerization states: (i) as partially crosslinked polymers in liquid form, which is the usual condition that the UF resins are available on the market and (ii) as partially cured polymers in solid form. The partially cured resins were prepared by drying the liquid resins in a convection oven at 120 °C for 2 h. During the drying process, the curing of the resin is progressed and a three-dimensional network is built up corresponding to that developed during the production of wood-based panels. This process is irreversible and results in an insoluble resin. The FTIR transmittance spectra were obtained with a Spectrum 1000 Perkin-Elmer spectrometer in the spectral area of 400–4000 cm⁻¹, with a resolution 2 cm⁻¹ and 32 scans. For the resins in liquid form, the sandwich preparation method was used, in which a drop of hybrid is placed between two KBr pellets of 110 mg each. For the FTIR measurements of solid samples, KBr pellets with 1 wt% of the powdered material were produced.

2.4. Scanning electron microscopy (SEM)

The morphology of the prepared samples was examined in a SEM system (JEOL JSM 840A-Oxford ISIS 300 microscope). The samples were carbon coated in order to provide good conductivity of the electron beam. Operating conditions were: accelerating voltage 20 kV, probe current 45 nA, and counting time 60 s.

2.5. X-ray diffraction (XRD)

XRD analysis was performed on the solid UF hybrids using a Rigaku Ultima⁺ diffractometer using Cu K α radiation, a step size of 0.05° and a step time of 3 s, operating at 40 kV and 30 mA.

2.6. Differential scanning calorimetry (DSC)

DSC measurements were carried out in a Setaram DSC-141 calorimeter. Temperature and energy calibrations of the instrument were performed for different heating rates, using the well-known melting temperatures and melting enthalpies of high-purity Zinc (Zn), Tin (Sn) and Indium (In) supplied with the instrument. Resin mixtures of 6 mg were placed in stainless steel sealed or open aluminium crucibles, depending on the desirable conditions, while an identical empty crucible was used as reference in each measurement. The samples were heated from ambient temperature (25 °C) to 210–230 °C in a 50 ml/min flow of N₂. The used heating rates were 2.5, 5, 10 and 15 °C/min.

2.7. Thermogravimetric analysis (TGA)

The TGA study was carried out with a SETARAM SETSYS 16/18 TG-DTA. Samples (6 ± 0.2 mg) were placed in alumina crucibles. An empty alumina crucible was used as reference. The samples were heated from ambient temperature to 500 °C in a 50 ml/min flow of N₂ with a heating rate of 5 °C/min.

2.8. Application of UF resins into wood-based panels and their characterization

The bonding ability of the resins was tested in the production of particleboard panels in the premises of Chimar Hellas company. The testing of the panels was carried out according to the relative EU standards as described by Zorba et al. [19].

3. Results and discussion

3.1. Characterization of resins, interactions with SiO₂ nanoparticles

The chemical structure of UF resins can be specified as poly(methylene methylene ether hydroxymethylureas) which are resulted by the condensation reactions of urea with aqueous solution of formaldehyde. Fumed SiO₂ nanoparticles have surface silanol groups (Si-OH) which can react with macromolecular end groups and mainly with hydroxyl groups via condensation reactions [20]. During the first step of addition reactions between urea and formaldehyde 1,3-bis(hydroxymethyl) urea (dimethylolurea) is produced, which has 2 hydroxyl groups and could interact with silanol groups of SiO₂. In order to verify this during the formation of UF/nanoSiO₂ hybrids all samples were studied with FTIR spectroscopy and the recorded spectra are shown in Fig. 1.

The multiple and broad peaks on the UF-0 resin's spectra are mainly due to the complexity of the polymer structure. In the spectrum of the liquid UF resin, the broad peak around 3350–3450 cm⁻¹ can be attributed to the hydrogen bonded O–H and N–H. The fact that this band is rather broad may be attributed to monomers such as water and formaldehyde, whose O–H group may form hydrogen bonds with reactive functional groups as CH₂OH, NH₂ and NH [21]. Also, it is important to mention that the free –NH₂ group has a characteristic peak at 3440 cm⁻¹, while the bonded –NH group at 3340 cm⁻¹. The fact that in the spectrum of the pure UF resin, the peak is centered at the area of 3360 cm⁻¹, indicates that the amount of bonded –NH is higher compared to the free –NH₂. In the area of 1600–1650 cm⁻¹ multiple and some overlapped peaks

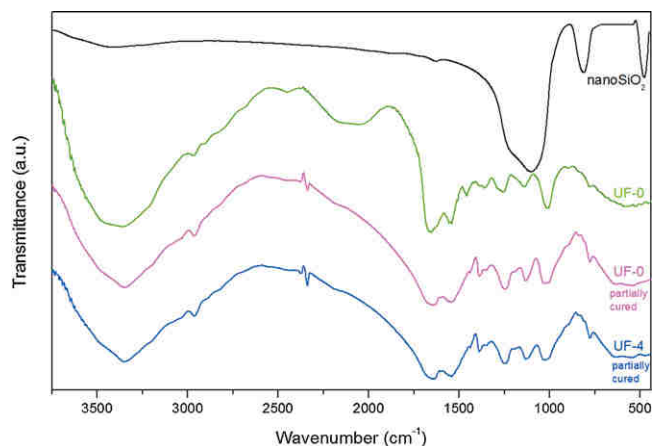


Fig. 1. FTIR transmittance spectra of SiO₂ nanoparticles, UF-0 resin, UF-0 and UF-4 partially cured resins.

appear in the spectrum of pure UF resin. These peaks are assigned to the C=O stretching of amide I and II, as well as the –N–H scissoring of amide I. The overlapped peaks at the area 1500–1600 cm^{−1} are attributed to –N–H bending vibrations of amide II. The multiple peaks at 1460–1470 cm^{−1} may be attributed to C–H bending vibrations of CH₂–N group, while the small peaks at the area of 1320–1450 cm^{−1} can be assigned to stretching C–N vibrations of amide I and II, while it has also been assigned to C–H stretching and –O–H bending vibrations of alcohol [22]. The strong but broad peak at 1255 cm^{−1} is assigned to C–N stretching vibrations of amide II [23]. The 1139 cm^{−1} peak is attributed to both the asymmetric stretch of >

[24]. The strong 1010 cm^{−1} peak is due to C–C–O stretching mode of CH₂OH and finally, the weak small peak at 770 cm^{−1} is due to –N–H bending and wagging vibrations of amide I and II respectively [22].

The transmittance spectrum of the solid UF-0 resin, is shown in Fig. 1. As can be seen there are some differences in the FTIR spectra of the resin before (UF-0) and after curing (UF-0 partially cured). The peak at the region of 3350 cm^{−1} seems to be a lot sharper in the cured resin, which indicates a reduction in the extent of hydrogen bonded interactions, which is expected as the structure becomes cross-linked [23]. Also, the peak at 2960 cm^{−1} becomes sharper and more distinct, which along with the absence of the 2900 cm^{−1} peak of the asymmetric C–H alcohol stretches, indicates that quantity of ether and methylene linkages is increased in cured resin and thus, a cross-linking process has evolved. This assumption can further be supported by the sharpening of 1130 cm^{−1} and the shifting and broadening of the 1024 cm^{−1} peak which is also due to ether bond vibrations [25].

The spectrum of nanoSiO₂ exhibits a characteristic peak at 1000–1200 cm^{−1}, which is due to the asymmetric stretching vibrations of Si–O–Si, as well as the 812 and 472 cm^{−1} ones which are attributed to the symmetric stretching and bending of Si–O–Si respectively [22].

The recorded spectra of all hybrids are almost identical and for this reason in Fig. 1 only the spectrum of the sample containing 3.5 wt% nanoSiO₂ (UF-4) is presented. As can be seen, compared with the neat UF-0, there is a difference in the broadness and the position of the peak at the area of 3350 cm^{−1} which is shifted to lower wavenumbers indicating the formation of hydrogen bonds between the silanol group of nanoSiO₂ and the polymer chain. However, this shift is very small in order to safely extract conclusions. Maybe because the nanoSiO₂ content is very small (maximum 3.5 wt%) and thus the extend or interactions is in the area of instrumentation error. For this reason the resins

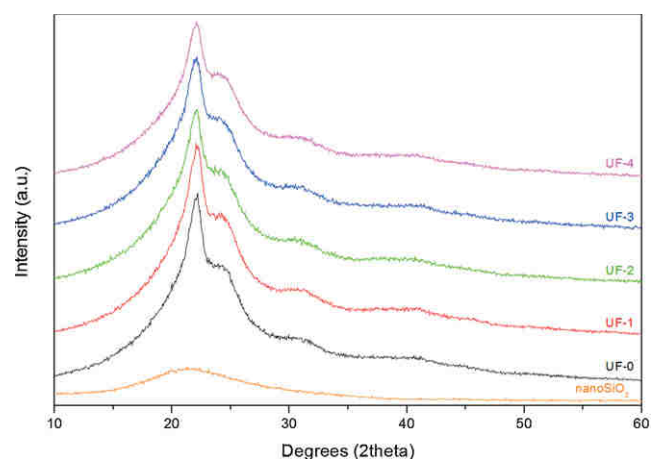


Fig. 2.

The XRD pattern of pure nanoSiO₂ consists of a broad diffraction peak at 22°, which is a proof that it is an amorphous material, while that of pure UF resin presents a relatively sharp peak at 22° along with three broader peaks at 24°, 31° and 41°, as also reported in the literature [17]. The XRD patterns of all samples, confirm the fact that all the resins are mainly amorphous with a small degree of order, while the presence of nanoSiO₂ cannot change the appearance of the patterns. Only in UF-3 and UF-4 patterns, the peak at 22° seems to be slightly broader than in UF-0, which can be due to the presence of nanoSiO₂ and the higher degree of amorphisation of the material.

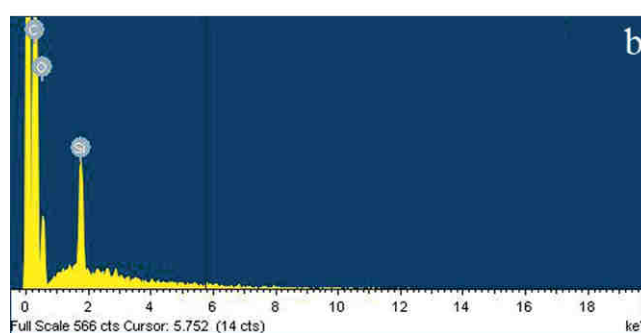
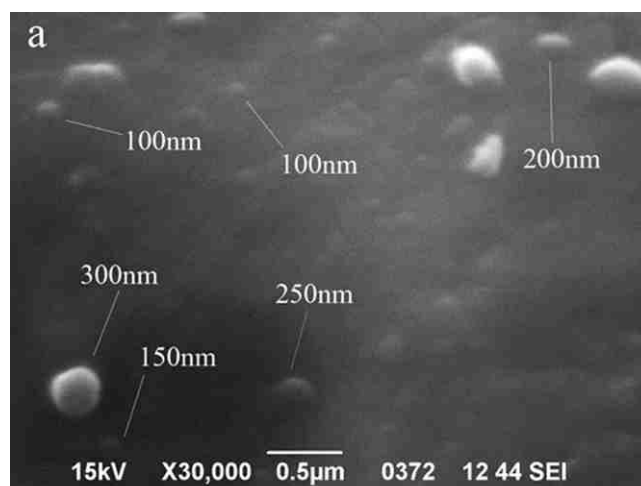
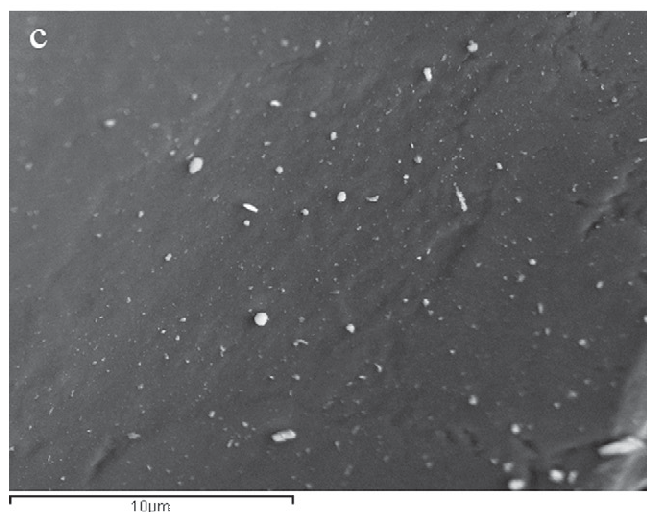
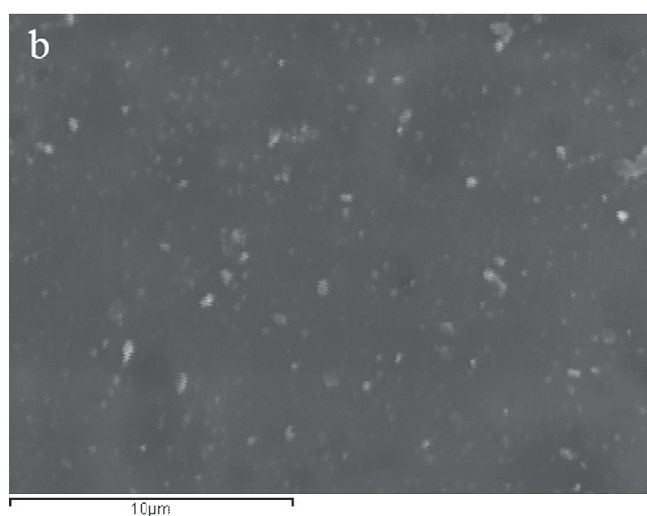
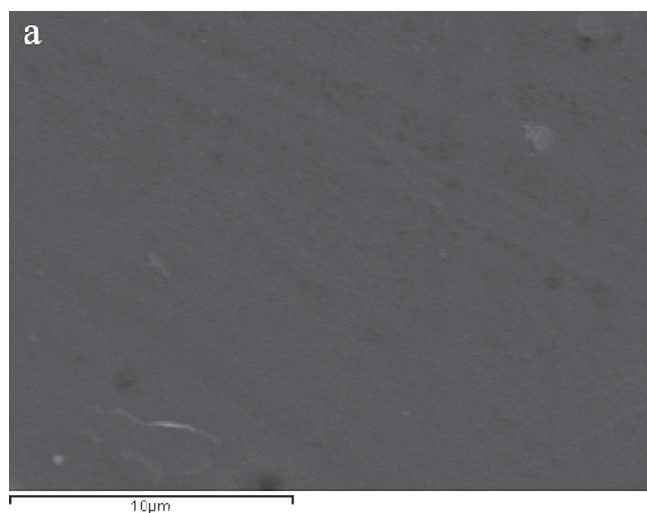
The surface morphology of the resins was studied with SEM/EDS. All the pictures were taken with 5000× magnification. In the case of the resins, some characteristic microphotographs of the samples UF-0, UF-2 and UF-4 are presented in Fig. 3. These pictures show that as the nanoSiO₂ concentration increases, greater number of small bright areas appear on the samples. The EDS analysis revealed that the bright spots are SiO₂ nanoparticles and so, as the nanoSiO₂ concentration increases, the nanoSiO₂ spots seem to become larger and more apparent.

In order to inspect the size of the aggregates formed by the nanoparticles, the microphotographs were studied in higher magnification as shown in Fig. 4, where also a characteristic EDS spectrum is presented. In that figure, the nanoSiO₂ aggregates formed, can clearly be seen. From these figures it can be concluded that the average size of the aggregates is almost 150 nm, while smaller and larger particles were also present, ranging between 50 and 350 nm. The size of these aggregates depends on the nanoSiO₂ content and increases as the SiO₂ content is increased.

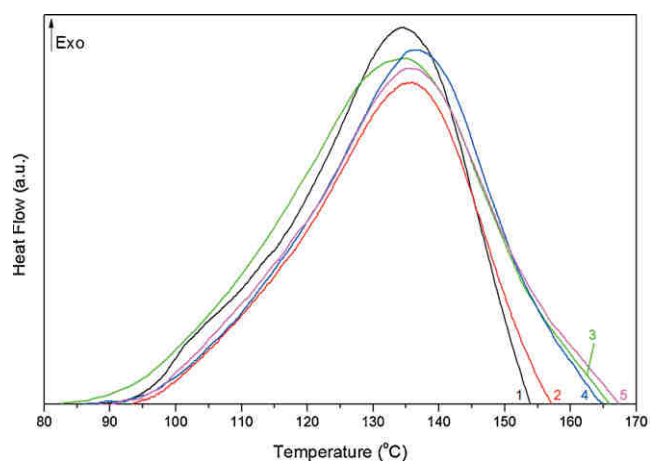
The presence of additives as SiO₂ can differentiate the condensation reactions. This is due to the presence of silanol groups in nanoSiO₂ surface, which are highly reactive and can form hydrogen bonds, as was verified from FTIR spectra, or participate in condensation reactions. For this reason, curing reactions of UF in the presence of additives is an attractive object for research.

3.2. Effect of SiO₂ nanoparticles on curing reactions of the resins

In the present study, DSC analysis was used to study curing reactions of UF/nanoSiO₂ hybrids. In Fig. 5 the DSC curves of all samples during curing for heating rate of 2.5 °C/min, are presented. It is revealed that all resins follow the same curing trend. In the case of neat UF-0 the maximum peak temperature is recorded at



[26]. Kissinger's equation (1) assumes that the reaction rate reaches its maximum at the temperature (T_p) of the



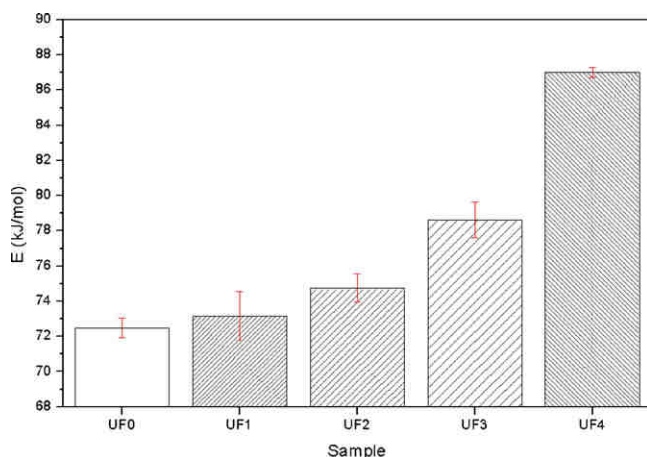


Fig. 6. Values of activation energy calculated for every sample using Kissinger's method.

DTG peak and that the degree of conversion (α) at T_p is constant, although that does not apply in every case.

$$\ln \left(\frac{\beta}{T_p^2} \right) = -\frac{E}{RT_p} + \ln \left(\frac{AR}{E} \right) \quad (1)$$

In Eq. (1) β is the heating rate, E is the activation energy, R is the gas constant and A is the pre-exponential factor. The results of the kinetic analysis are shown in Fig. 6 and the Kissinger plot is pictured in Fig. 7, where the values of R^2 that show the quality of the fitting are also pictured. The values of activation energy are in the same range as those previously reported in the literature [5]. The calculated activation energy, slightly increases as the concentration of nanoparticles increases. A total deviation of almost 20% is noted between samples UF-0 and UF-4. It is known from literature that when SiO_2 nanoparticles are introduced into a polymeric material, they tend to form bonds with the backbone chains [17,25,27]. This can also be concluded from our FTIR and DSC study as higher activation energies were found for hybrids with higher nanofiller concentration. Since the nanoparticles form hydrogen bonds with the polymer chain, an altered interphase is created around each particle or aggregate. As a result, the mobility of the polymer chain that is needed in order for the polymer to cure, is less in samples with higher amount of nanoparticles and therefore, they need more energy for the crosslinking process. Furthermore, nanoparticles behave as a physical obstacle disrupting the continuity in the matrix and therefore, making it more difficult for the reactive

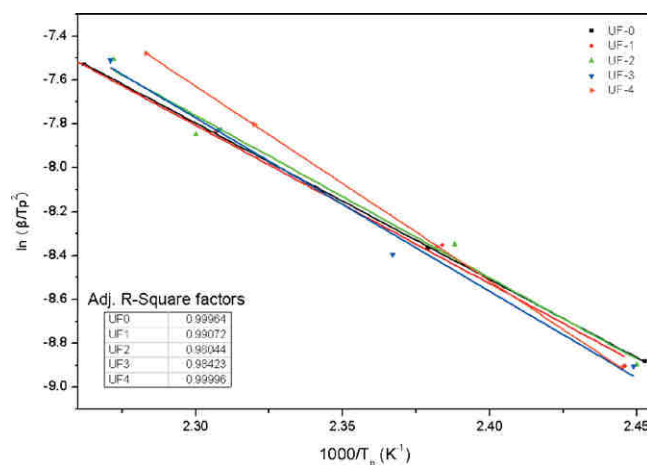


Fig. 7. Kissinger's plot for all studied samples.

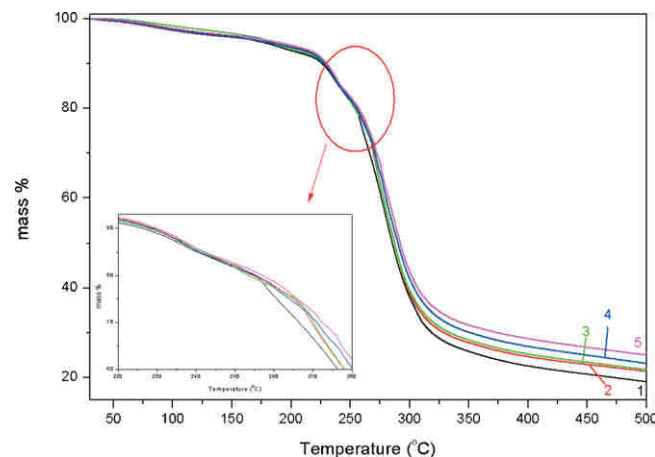


Fig. 8. TG curves of all samples: (1) UF-0, (2) UF-1, (3) UF-2, (4) UF-3, and (5) UF-4. Heating rate 10 °C/min.

groups of urea and formaldehyde to come close and interact. Thus, the higher activation energies along with the slightly higher peak temperatures of the curing are an indication of the existence of polymer–nanoparticle interactions.

3.3. Effect of SiO_2 nanoparticles on the thermal stability of the resins

Nano SiO_2 when added in a polymer matrix have as result to enhance the thermal stability of different polymers [28,29]. This was also expected in the present study and in order to evaluate this thermogravimetric analysis was used. In Fig. 8 the TG curves for all samples are presented, revealing that the addition of nano SiO_2 to the UF resin do not affect its thermal stability. From the TG curves it is clear that the study can be divided into two regions [30]. The first mass loss step that corresponds to 3–4.5% losses in every case, occurs for all samples between 50 and 100 °C. This step corresponds to water evaporation of the samples. Slow formaldehyde emissions at temperatures 100–200 °C, result in small mass losses, in every sample. Above 200 °C, the main degradation step is initiated when chain scissions begin and the radicals formed induce the formation of cyclic structures in the polymer chain. This process results in the extensive polymer fragmentation. Degradation of cured resins begins with release of formaldehyde from dimethylene ether groups [24] and the maximum degradation rate happens when the stable methylene ether linkages deconstruct [31]. Comparing the mass loss curves of all samples above 200 °C, it can be seen that the hybrids do not affect the thermal stability of the resin. In details, 30% mass loss occurs in pure resin at 266 °C while in UF-4 hybrid at 272 °C and 50% mass loss occurs at 285 for UF-0 and at 292 °C for UF-4 hybrid. With such small deviations in the TG curves it is very hard to study the effect of SiO_2 on the resins, and it is not safe to say that nano SiO_2 enhance the thermal stability of the system. The other resins with lower SiO_2 content have intermediate values between those of UF-0 and UF-4, which are in all cases slightly higher than UF-0. Nanoparticles tend to have a shielding effect on the emission of decomposition products, as was also found in our previous studies in different polymers [28], however this cannot be confirmed from our study as there is not definite thermal stabilization of the system. This could be due to insufficient dispersion caused by the choice of mechanical stirring as a preparation technique and also, because the amounts of the nanoparticles used were rather small (maximum 3.5 wt%). Also, the fact that SiO_2 is thermally stable for temperatures up to 500 °C [32], results in the increasing residual of the heated samples with higher nanoparticle concentrations.

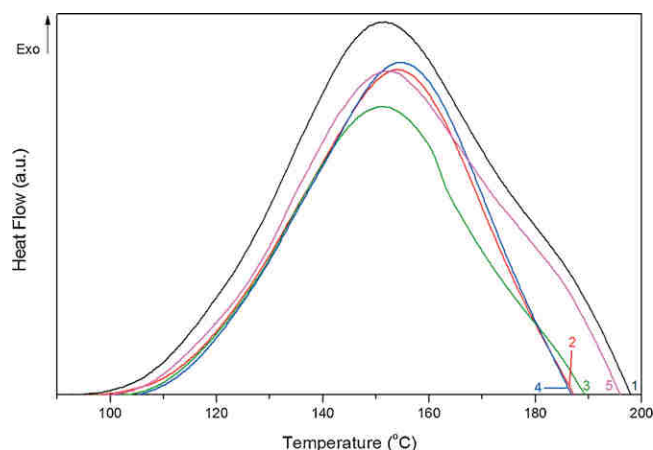


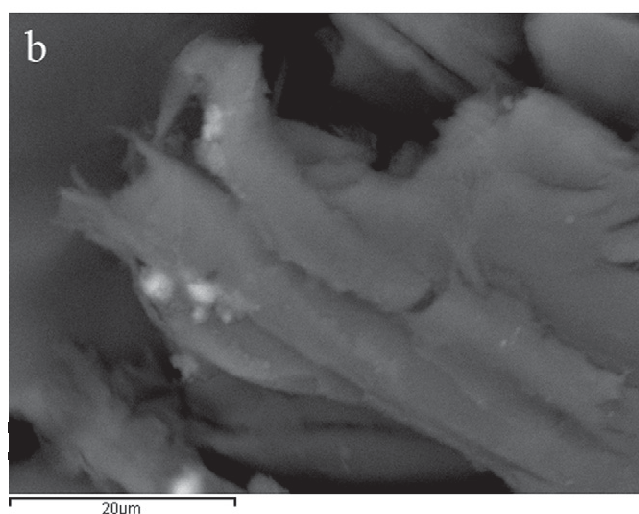
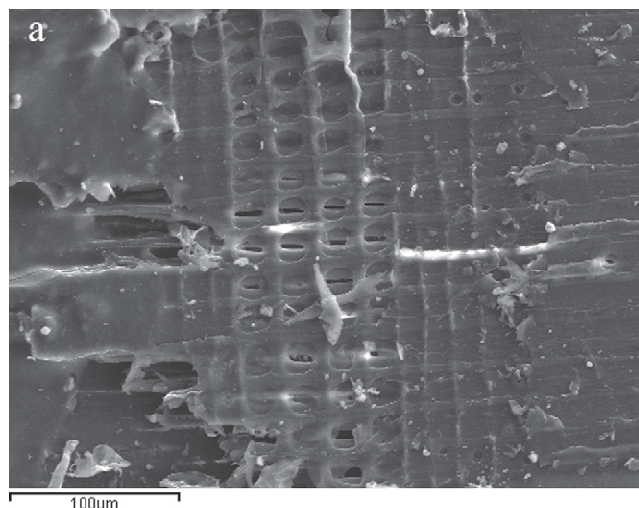
Fig. 9. DSC curves of all samples mixed with wood particles: (1) UF-0, (2) UF-1, (3) UF-2, (4) UF-3, and (5) UF-4. Heating rate 10 °C/min.

3.4. Effect of SiO₂ nanoparticles on the properties of wood-based panels

From the thermal analysis it was found that the addition of SiO₂ nanoparticles retards slightly the condensation reactions during the crosslinking procedure for the formation of UF resins. An analogous effect could also be observed in the application of these resins in the wood panels and for this reason the effect of interactions of the hybrids with UF resins and wood particles was also examined. A few milligrams of wood particles were mixed with each of the resins and all the DSC curves obtained are presented in Fig. 9. As can be seen from the DSC curves, UF-0 sample presents the lowest peak temperature compared to hybrids. This means that when the resins are mixed with wood particles they follow the same trend as when studied without wood presence: nanofillers slightly inhibit the curing process and as a result the peak temperature is shifted to higher temperatures compared to neat resin.

The dispersion of SiO₂ nanoparticles in wood panels was also studied. In Fig. 10 characteristic pictures of the UF-4 mixture with wood (pine) particles with low and high resolution are presented. From the microphotographs in Fig. 10 it can be seen that the wood is covered with the resin at various types of sections. This is evidence of a good penetration of resin into the wood structure. From Fig. 10b, it is obvious that nanoparticles tend to lie on the rough edges of the wood particles (white spots identified with EDS analysis). Also in this case SiO₂ nanoparticles tend to form aggregates as in neat resins. This could have a negative result in the mechanical properties of the formed panels. Thus, the bonding ability of the resins was tested in the production of particleboard panels.

Besides thermal properties and SiO₂ dispersion of wood panels other properties were also evaluated. The testing of the panels was carried out according to the relative EU standards as described by



[19]. The particleboards were produced at two different pressing times and their properties are shown in Table 1. The results of their testing manifest that the mechanical properties of the panels, like the internal bond and the modulus of rupture, are slightly increased with the use of nanoSiO₂. The thickness swelling is also improved compared to the standard resin, especially at the low nanoSiO₂ levels, indicating that no high concentration of nanoSiO₂ is required for this improvement. The free formaldehyde emissions are just lower compared with neat UF in all hybrids. However the reduction is very small and practically free formaldehyde remains unaffected by the addition of SiO₂ nanoparticles. Theoretically, free

Table 1
Specifications and properties of the produced resins.

Resin	UF-0	UF-1	UF-2	UF-3	UF-4
Short press time					
Internal bond (MPa)	0.65	0.71	0.72	0.70	0.66
Thickness swelling 24 h, 20 °C (%)	29.63	27.07	27.15	27.39	28.41
Modulus of rupture (MPa)	13.60	15.09	14.77	14.52	14.81
Moisture content of board (%)	6.88	7.31	6.97	6.77	6.66
Free formaldehyde at 6.5% moisture (mg/100 g wood)	6.01	5.97	5.97	5.99	5.96
Long press time					
Internal bond (MPa)	0.66	0.66	0.68	0.76	0.66
Thickness swelling 24 h, 20 °C (%)	30.56	26.07	27.49	29.37	29.00
Modulus of rupture (MPa)	12.83	14.58	13.32	15.05	15.21

formaldehyde content was expected to be noticeably reduced in the presence of nanoSiO₂, due to the shielding effect that nanoparticles could have. However, this was not found possibly because the amounts of the nanoparticles used were rather small (maximum 3.5 wt%) and the dispersion was not perfect.

4. Conclusions

The ultimate goal of the nanoSiO₂ addition is to improve the properties of the UF resin. The degree, to which this is done, strongly depends on the dispersion of the additive into the resin and the resin–wood adhesion. In this particular work, it was verified from FTIR spectroscopy that SiO₂ nanoparticles can create hydrogen bonds with UF resins. This was also verified from DSC analysis since the peak curing temperatures and the activation energies of the hybrids was found to be slightly higher than those of the pure resin, which implies the formation of bonds between the nanoSiO₂ and the polymer chains. The same effect on curing temperatures was also found on mixtures of resin with wood particles, implying the formation of bonds between nanoSiO₂ and polymer chain in wood presence too. However, this is not effective in order to have a fine dispersion of SiO₂ nanoparticles as individual particles in the polymer matrix and some aggregates are also formed. Furthermore, nanoSiO₂ as an additive in UF resins, was found to affect many of the hybrids' properties, when they are applied to particleboards, such as internal bond, thickness swelling and modulus of rupture.

Since the industry requires compromises between the best performance and the lowest cost of such materials and considering the low amount of nanofillers and the low cost and fast preparation method that was performed in the present work, the results of this study are considered satisfactory. From this work, it has been shown that SiO₂ nanoparticles are promising materials for the improvement of the UF resin performance and so, further studies to this direction are worthwhile.

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