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산화전분과 표면개질된 나노 SiO_2가 Urea-Formaldehyde 수지의 성능에 미치는 영향

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Influence of Oxidized Starch and Modified Nano-SiO_2 on Performance of Urea-Formaldehyde (UF) Resin

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Abstract: In this work, the nano-SiO_2 was firstly modified by silane coupling agent (3-aminopropyltriethoxysilane), meanwhile the dispersion of nanoparticles was studied with transmission electron microscope (TEM). Then urea-formaldehyde (UF) resins were synthesized and modified with the compound modifier made of different ratio of modified nano-SiO_2 and oxidized starch. All the products were characterized with Fourier transform infrared spectroscopy (FTIR). Free formaldehyde content and bonding strength were measured as the main standard of the performance of the resin. The other performances of modified UF resins were also analysized by X-ray diffractometry (XRD) and scanning electron microscopy (SEM). The results showed that the modification could effectively reduce the free formaldehyde content, from 0.49 to 0.19%, and enhance the bonding strength, from 0.90 to 2.06 MPa.

Keywords: urea-formaldehyde resin, silane coupling agent, oxidized starch, free formaldehyde content, nano-SiO_2.

Introduction

Urea-formaldehyde (UF) resins are one of the most widely used wood adhesives with wide applications in the manufacture of wood-based composite panels, such as plywood, particleboard and medium-density fiberboard.[1-3] As a kind of wood adhesives, the UF resins have several advantages, including lower price, high reactivity and good adhesion to wood.[4,5] Furthermore, nonflammability and colorlessness promote the continued use of this resin in the wood industry. Just like every coin has two sides, the drawbacks of UF resins are also very obvious, such as higher free formaldehyde content and poor bonding strength under high humidity.[6,7] Formaldehyde is known as one of the main factors causing pollution of indoor environment, and it also endanger the people's health and living of the interior decoration. Therefore, how to reduce the content of free formaldehyde has been one of the most important aspects of UF resin research.[8] One rather common approach in order to reduce formaldehyde emission is to lower F/U molar ratio of the synthesized resin.[9] However, this leads to a decrease of mechanical strength and water resistance. Adding additives is another effective method which has been used so far.

Melamine is one of the most generally employed modifiers in the synthesis of UF resins, which can reduce the formaldehyde emission and improve water resistance of the adhesive.[10] Also, phenol and polyvinyl acetate are also applied as formaldehyde scavengers. Nowadays, with the development of new technology, new additives have been discovered gradually. Among these modifiers, nano-SiO_2 has attracted a wide range of attention because of its large surface areas which can bring on new properties or even modify important properties of the resins. But nano-SiO_2 has a high surface energy, which makes it in a state of thermodynamic instability, and it is very easy to aggregate.[11,12] Therefore, the surface modification of nano-SiO_2 is necessary. Also nano-SiO_2 is expensive, which is contradictory to the low-cost concept of industry. As a natural

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polymer, starch has been widely used in industry for a long time, due to its low cost, biodegradability and renewability.[13-15] Moreover, starch contains a large number of hydroxyls, part of which will be converted to aldehyde groups and carboxyl groups after oxidation. These new groups of oxidized starch can react with free formaldehyde and UF resin, which can reduce the free formaldehyde content and improve the bonding strength.[16] Besides, the production cost of UF resin can be reduced obviously by introducing oxidized starch into the resin system.

In this part of work, we selected the composite modifier composed of oxidized starch and modified nano-SiO_2 to modify UF resin, which has not been seen in previous studies. The modified nano-SiO_2 and oxidized starch can react with free formaldehyde and UF resin. Besides, the low price of oxidized starch also greatly reduced the overall cost of the modification. The whole study process began with the modified nano-SiO_2. Nano-SiO_2 was modified by silane coupling agent (3-aminopropyltriethoxysilane) firstly. Also, the modification result of nano-SiO_2 was anlysized by TEM and laser particle analyzer. Then, a series of modified UF resins were synthesized by adjusting the ratio of the compound modifier composed of oxidized starch and modified nano-SiO_2. At the same time, the structure and performance of the hybrids were thoroughly performed using titration analysis, mechanical testing, FTIR, SEM and XRD.

Experimental

Materials. Urea (≥99.0%), formaldehyde (37%) and nano-SiO_2 (≥99.5%, 15 nm) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China), ammonium chloride (AR), sodium hydroxide (AR), toluene and 3-aminopropyltriethoxysilane (KH-550, AR) were supplied by Tianjin Kermel Chemical Reagent Co., Ltd (Tianjin, China). Oxidized Corn Starch was purchased from Shanghai Luan Biological Technology Co., Ltd (Shanghai, China).

Modification of Nano-SiO_2. Some of nano-SiO_2 was added into toluene and gave it an ultrasonic dispersion for 30 min, then the reaction system was placed in an oil bath at 80 ºC, at this time, silane coupling agent (KH-550) and deionized water which account for 20% and 70% of the mass fraction of nano-SiO_2 respectively were added to the system of toluene, at last, the stirrer was set to a strong rate and kept for 120 min. The dispersion of nano-SiO_2 was filtered, dried and ground to obtain a modified nano-SiO_2.

Synthesis of UF Adhesive Modified with Modified Nano-SiO_2 and Oxidized Starch. Liquid UF resin was prepared in the laboratory following conventional alkaline-acid-alkaline three-step reaction by adding the 3rd urea. The total molar ratio of formaldehyde and urea was 1:1.2. Firstly, a certain amount of formaldehyde solution was poured into the three-neck flask which equipped with condenser and thermometer and adjusted its pH to 8.2~8.5 with 10% NaOH. The first part of urea and the mixture of varying proportions of oxidized corn starch and nano-SiO_2 were added at 40 ºC, heated to 90 ºC within half an hour and kept for 30 min. Next, adjusted the pH of the system to 4-5 with 10% NH_4Cl solution, then the reaction was continued for about 25 min. The system was cooled to 80 ºC and added the second batch of urea and kept for another half an hour. Finally, adjusted the pH to 8-9, cooled to 70 ºC, added the remaining urea and kept reacting for 30 min. When the temperature dropped to 40 ºC, the modified UF resin could be obtained. The composition and basic properties of UF resins are summarized in Table 1.

Preparation and Testing of Plywood. Three-layer plywood panels of dimensions 300×300×1.5 mm were prepared using white birch veneers with lower moisture content. The UF resin which was mixed with 1 wt% ammonium chloride and 5 wt% corn starch was applied to both sides of the veneer at the amount of 350 g/m^2. After that, the veneers were allowed to age for 20 min, then the veneers were pre-pressed at room temperature and 1.0 MPa for 30 min and then hot pressed at 120 ºC and 1.5 MPa for 3 min.

Characterization. The fourier transform infrared (FTIR) spectroscopy was tested on the spectrum-400 infrared spectrometer (PE, USA) in the region 400-4000 cm^{-1}. Specimens were prepared by grinding the sample with KBr (mass ratio 1:200).

The particle distribution of ordinary nano-SiO_2 and modified nano-SiO_2 were analyzed by Mastersizer 2000 laser particle size analyzer (Malvern, England). The microstructure of the nano-SiO_2 was observed by the JEM-2100 transmission electron microscope (JEOL, Japan). The microstructure of the resin was obtained using JSM-7500F scanning electron microscopy (JEOL, Japan).

According to the method of GB/T 14074, the free formaldehyde content of the resin was calculated by titration. Adhesive bonding strength was measured in accordance with standard of GB/T 9846.

The X-ray diffraction (XRD) pattern of resin was acquired using a D/max-2200VPC diffractometer (Rigaku Corporation,

Japan) at 2θ from 10° to 60° and a scanning speed of 20°/min.

Results and Discussion

Analysis of the Particle Size and Surface Micromorphology of Nano-SiO_2. As can be seen from Figure 1, the particle size distribution of pure nano-SiO_2 is wide and dispersive, and the most of the aggregate size is larger than 100 nm. In comparison, the aggregate diameter of modified nano-SiO_2 significantly narrowed and the diameter mainly concentrated in 70~100 nm. All of these facts mean that the aggregation of nano-SiO_2 modified by KH-550 silane coupling agent is greatly weakened, and the system stability is also enhanced.

The transmission electron microscopy images of pure nano-SiO_2 and modified nano-SiO_2 are shown in Figure 2(a) and (b), respectively. It can be seen that the aggregation of the ordinary nano-SiO_2 is more serious, meanwhile the size of the particles is relatively large, which is consistent with the test results of particle size analyzer. This may be ascribed to the higher surface energy of unmodified nano-SiO_2 which made it easy for nano-SiO_2 to react with water molecules in air and form the hydroxyl group (-OH). On the contrary, the aggregation of nano-SiO_2 modified by silane coupling agent is obviously receded. This is mainly due to the bonding or adsorption of silane coupling agent on the surface of nano-SiO_2. The reaction forms an organic adsorption layer on the surface of the particles, which reduces the surface energy of nano-SiO_2 and aggregation.

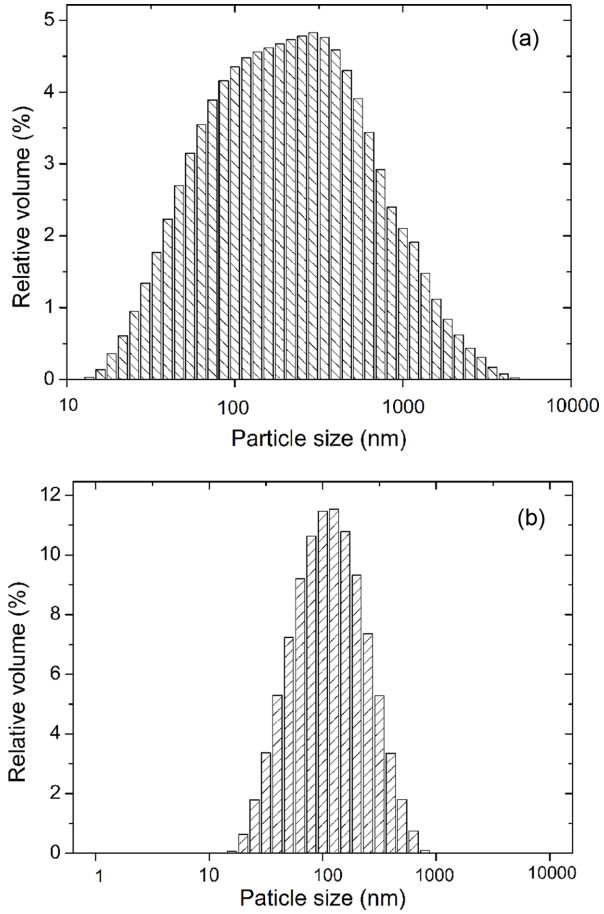


Figure 1. Particle size of pure (a); modified (b) nano-SiO_2.

FTIR Analysis. Figure 3(a) is the infrared spectra of nano-SiO_2 and KH-550 modified nano-SiO_2. As shown in Figure 3(a), peak near 3100-3700 cm^{-1} belongs to the stretching vibration peak of -OH and -NH groups. The spectrum of nano-SiO_2 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} which are attributed to the symmetric stretching and bending of Si-O-Si respectively. Compared with pure nano-SiO_2, there are new characteristic absorption peaks at 1505 and 2928 cm^{-1}, which correspond to the C-C vibration peak and -CH_3, -CH_2 vibration peak respectively. It proved that the nano-SiO_2 had reacted with silane coupling agent KH-550.

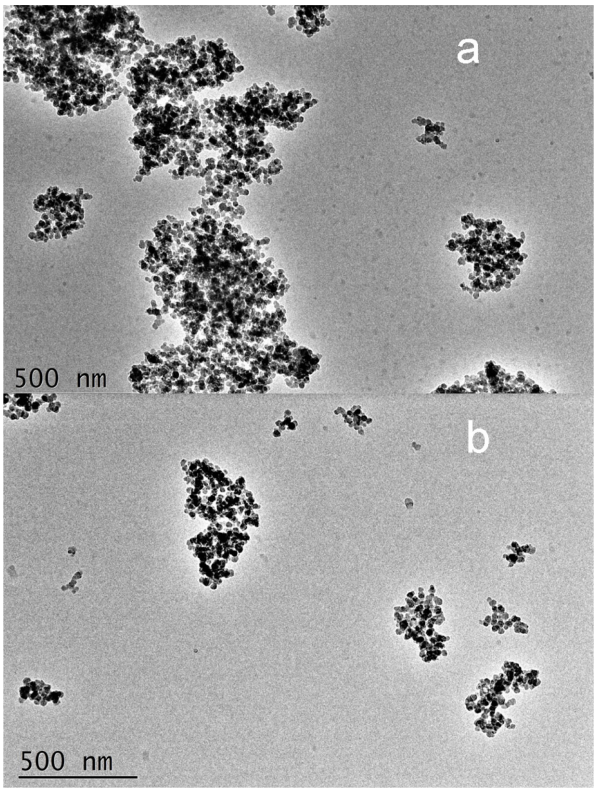


Figure 2. TEM microphotographs of pure nano-SiO_2 (a); modified nano-SiO_2 (b).

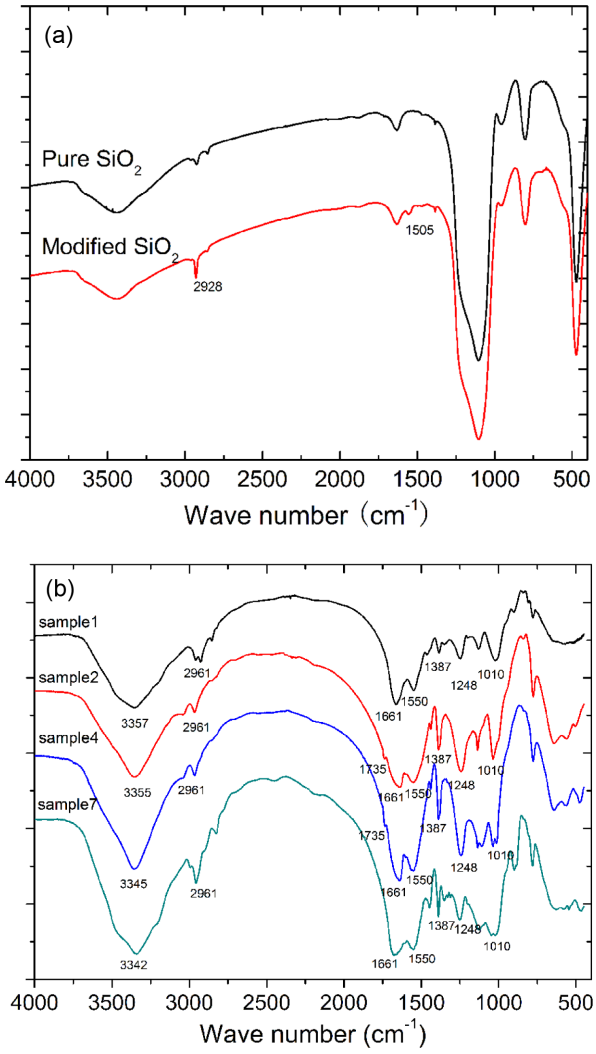
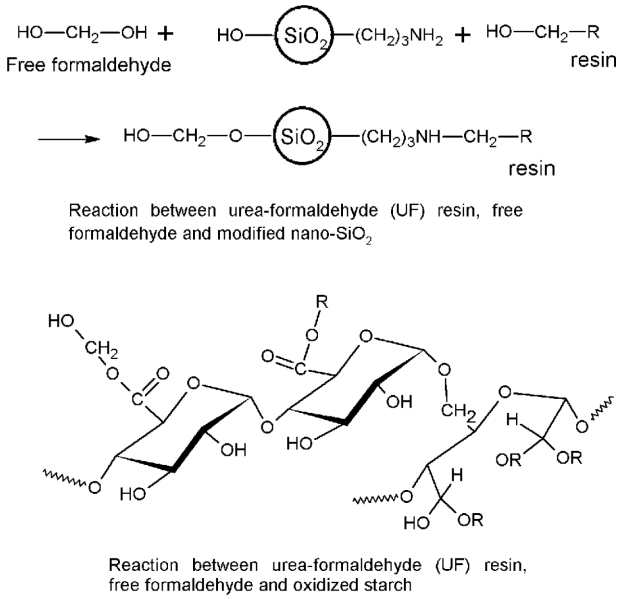


Figure 3. FTIR spectra of nano-SiO_2 (a); urea-formaldehyde (UF) resins (b).

Figure 3(b) is the infrared spectrum of pure (sample 1) and modified (sample 2, sample 4 and sample 7) UF resins. All FTIR curves exhibit the characteristic stretching vibration peaks O-H between 3700 and 3100 cm^{-1}.[17,18] Besides, stretching peaks of C-H at 2961 cm^{-1} belongs to methylene. The peaks at the 1550 and 1661 cm^{-1} are attributed to N-H bending vibrations of amide. The peaks at 1387 and 1248 cm^{-1} reflect the in-plane deformation vibration of the methylene. What's more, the obvious absorption peak of methylol group is also revealed at 1010 cm^{-1}. All of these characteristic absorption peaks show the typical characteristics of UF resin. Compared with pure UF resin (sample 1), the spectra of modified UF resins (sample 2 and sample 4) show a small peak at 1735 cm^{-1}. This may be attributed to the oxidized starch in these samples, which has



Scheme 1. Modification mechanism of urea-formaldehyde (UF) resin.

carboxyl group and can react with the free formaldehyde to produce the carbonyl group. The absorption peak of ester groups formed by oxidized starch and free formaldehyde and UF resins are coincident with the original absorption peaks, so these absorption peaks can't be reflected in the spectra obviously. In addition, the sample 4 and 7 also give a shoulder peak at the vicinity of 1010 cm^{-1}, which suggests that the UF resin has been reacted with the nano-SiO_2 and form the Si-O-C bond. As can be seen from the spectra of sample 4 and sample 7, compared with the sample 1, there are some differences at the broad peak between 3700 and 3100 cm^{-1} which is shifted to lower wavenumber indicating the formation of hydrogen bonds between the silanol group of nano-SiO_2 and the polymer chain.[19] These reaction mechanisms can be well reflected in Scheme 1.

Effect of Modification on the Basic Properties of UF Resin. Table 1 lists the basic properties of pure and modified UF resins, including appearance, viscosity and solid content. From Table 1, it can be gotten that the viscosity of UF resin increases with the increase of nano-SiO_2 mass, which is because of hydrogen bonds and Van der Waals force formed by the hydroxyl and amino groups between nano-SiO_2 and UF resin. This intermolecular force leads to an increase of the viscosity of the resin. But this enhancement will not influence the technology of sizing, on the contrary, it can prevent the diffusion of the adhesive and reduce the phenomenon of the glue

Table 1. Composition and Basic Properties of UF

Samples	Composition	Appearance	Viscosity (s)	Solid content (%)
Sample 1	1:1.62:0:0	Milk white	18.41	51.14
Sample 2	1:1.62:0.1:0	Milk white	21.18	55.44
Sample 3	1:1.62:0.08:0.02	Milk white	25.97	56.17
Sample 4	1:1.62:0.06:0.04	Milk white	26.66	55.77
Sample 5	1:1.62:0.04:0.06	Milk white	31.75	55.95
Sample 6	1:1.62:0.02:0.08	Milk white	33.37	55.30
Sample 7	1:1.62:0:0.1	Milk white	41.74	56.52

[a]The ratio arrangement sequence of composition is urea: formaldehyde solution: oxidized starch: modified nano-SiO_2 and these ratios are all mass ratio. [b]The viscosity is measured by No 4 Cup.

penetration or lack of glue line. At the same time, compared with the pure UF resin, solid content of modified UF resin was also increased. Although there is no law, the amount of the increase is almost the same, about 5%.

Analysis of Free Formaldehyde Content and Bonding Strength. As can be seen from Figure 4(a), compared with the ordinary UF resin, the free formaldehyde content of modified UF resin is greatly reduced. On the one hand, nano-SiO_2 has strong physical adsorption and chemical adsorption, which can form the hydrogen bond or covalent bond with free formaldehyde[20] and result in the reduction of free formaldehyde content; on the other hand, the oxidized starch contains hydroxyl groups, which can react with free formaldehyde and reduce the content of free formaldehyde of the resin. Figure 4(b) shows the bonding strength of the resins, from which it can be learned that the bonding strength data of all modified resins is improved when compared with the unmodified resin. Specially, the bonding strength of sample 5 reaches 2.06 MPa, much more than the blank sample (sample 1) of 0.90 MPa. This improvement is meanly attributed to the aldehyde and carboxyl groups of oxidized starch, which can react with the UF resin to form a cross-linked three-dimensional structure. These cross-linked structure makes winding between molecular chains become more serious. Besides, modified nano-SiO_2 is also easy to bond with the active groups of the UF resin, which can improve the cohesive force of the UF resin, simultaneously, the crosslinking reaction between nano-SiO_2 and hydroxyl groups of the wood surface also exist. All of these effects lead to a higher bonding strength of modified UF resins even under a condition of lower free formaldehyde content.

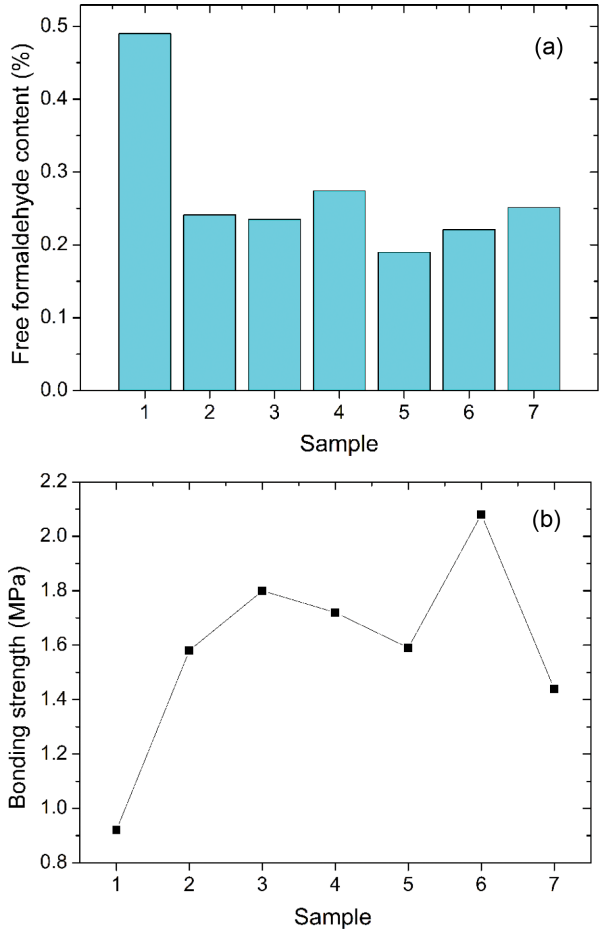


Figure 4. Free formaldehyde content (a); bonding strength (b) of sample 1 ~ sample 7.

X-ray Diffraction Analysis of Resins. Figure 5 shows the XRD patterns obtained from the resins of sample 1, sample 5 and sample 6. It can be seen from Figure 5 that all of these UF resins appear obvious diffraction peaks in 22°, which attributes to the interaction of the carbonyl group and the amino hydrogen bond (N-H…O=C) of UF resin and the formation of the layered semi-crystalline structure caused by the regular arrangement of this hydrogen bond.[21] This type of XRD pat-

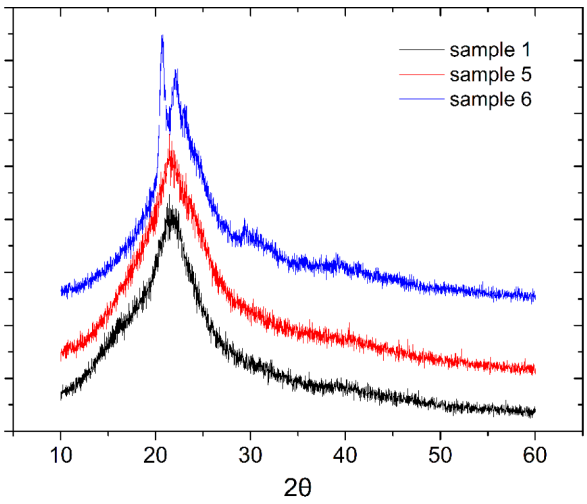


Figure 5. XRD patterns of sample 1, sample 5, and sample 6.

tern confirms the fact that all the resins are mainly amorphous with a small degree of order. But compared with the blank resin (sample 1), the diffraction peaks of the modified UF resins (sample 5 and sample 6) are slightly wider and weaker, which indicates that the presence of modifier (nano-SiO_2 and oxidized starch) slightly changes crystallization behavior of UF resin. The most possible reason is that the existence of silica and oxidized starch destroys the regularity of the carbonyl and amino groups.

Surface Micromorphology of Nano-SiO_2 and UF Resin. The SEM images of natural cross-section of sample 1, sample 5 and sample 6 are shown in Figure 6(a), (b) and (c). In the SEM images presented in Figure 6, cross-section of sample 1 is pretty smooth, whereas the sample 6 and sample 5 section is relatively rough. From the Figure 6(b) and (c), it can be found that there some white particles in the resins, which reflected a good combination between resin and nano-SiO_2 and oxidized starch. Simultaneously, the comparison result of Figure 6(b) and (c) implies that the modifier reduces the internal regularity of resin, which may change the crystal properties. This conclusion is also confirmed by the analysis of XRD.

Conclusions

The main purpose of this paper is to improve the performance of urea-formaldehyde (UF) resin by the introduction of the compound modifier which is made of modified nano-SiO_2 and oxidized starch. Among these performances, the free formaldehyde content and adhesive bonding strength are the two most important performances. In this particular work, it was

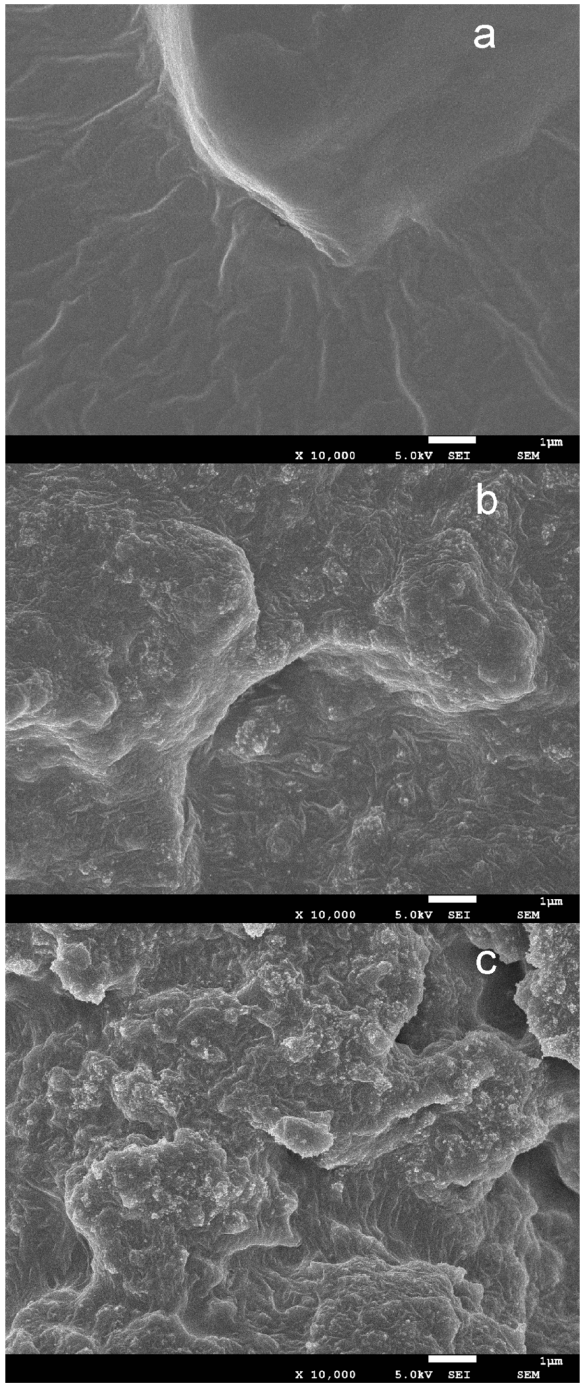


Figure 6. SEM microphotographs of sample 1 (a); sample 5 (b); sample 6 (c).

verified that the modification greatly reduced the free formaldehyde content of the resin, from 0.49 to 0.19%, at the same time, the bonding strength of the resin is improved obviously, from 0.90 to 2.06 MPa. These facts have proved that the oxidized starch and nano-SiO_2 can improve the main perfor-

mances of the UF resin. But the presence of oxidized starch and nano-SiO_2 breaks the regularity of amino and carbonyl groups in the resin, which leads to the decrease of the crystallinity of the resin.

In summary, the compound modifier composed of nano-SiO_2 and oxidized starch can improve the main properties of UF resin. But there are some drawbacks, for example, the viscosity of the resin is greatly increased, which can shorten the lifespan of the resin. So, further studies to this direction are worthwhile.

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