Hyperbranched Poly(amidoamine)s as Additives for Urea Formaldehyde Resin and Their Application in Particleboard Fabrication

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Three types of hyperbranched poly(amidoamine)s (PAMAMs), namely HB(MA-EDA)1, HB(MA-EDA)3, and HB(MA-DETA)1.2, were synthesized and used as modifiers for urea-formaldehyde (UF) resin. Particleboards bonded with these modified UF resins were fabricated and evaluated. The results showed that these PAMAMs caused some adverse effects on UF resin performance. The main problems of PAMAMs were their high buffer capacity and high pH values, which are attributed to the peripheral amino groups at the terminals, both of which had a serious negative influence on UF resin curing. These findings were supported by the gel time measurements in parallel with a predictive investigation on the resins using thermomechanical analysis (TMA). The gel time was prolonged, and the maximum modulus of elasticity (MOE) values decreased with the addition of HB(MA-EDA)3. The use of a strong acid curing agent (HCOOH) could reduce the gel time into a normal range; however the performance of the corresponding particleboards still deteriorated. Therefore, these PAMAMs are considered not suitable for the modification of UF resin when applied as final additives. Beyond all expectations, the modified UF resin that employed very finite amounts of HB(MA-EDA)1 as a pH regulator instead of NaOH yielded a considerable upgrade in performance of the produced particleboards.

Keywords: Hyperbranched poly(amidoamine)s; Urea formaldehyde (UF) resin; Particleboards; Additives

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INTRODUCTION

Dendritic polymers are a class of macromolecules with controlled surface functionality and size. The highly branched and three-dimensional architecture of these macromolecules have attracted considerable attention in the past few decades (Uhrich *et al*. 1992; Frechet 1994; Inoue 2000). In addition to numerous applications in various fields such as medicine, chemistry, materials science, biology, and physics, there is interest in the use of dendrimers as modifiers for wood adhesives (Essawy *et al*. 2009; 2010; Essawy and Mohamed 2011; Zhou *et al*. 2013; 2014). The dendritic poly(amidoamine)s (PAMAMs) are among the most widely used dendrimers as a result of their ready commercialization. Generally, PAMAM dendrimers are synthesized using a divergent synthesis approach according to Tomalia and co-workers (Tomalia *et al*. 1985), consisting of an ethylenediamine or ammonia as core initiators, a repeating monomer unit of polyamidoamine (–$CH_2CH_2CONHCH_2CH_2N$<), and terminal amino groups.

Modification of urea-formaldehyde (UF) resins with PAMAM dendrimers has proven to be an efficient way to upgrade their performance. Full, as well as half, of the generations of dendritic PAMAMs have been introduced into a UF wood adhesive system as modifiers (Essawy *et al*. 2009), revealing that PAMAMs are reactive modifiers for the UF wood adhesive system and can increase the stability of the UF resin and enhance the performance of the bonded wood joints. In addition, a series of core-shell PAMAM dendritic compounds bearing different end groups such as -OH, -NH_2, and $NH_3^{+-}Cl$ up to the third generation have been used as modifiers for UF resins (Essawy and Mohamed 2011). The results revealed that the prepared dendrimers had a reasonable surface activity, and the measurements suggested their ability to self-aggregate in water at very low concentrations and critical aggregation concentrations. The dendritic compounds proved to be effective as adhesion promoters for UF resins, which was ascribed in part to the improved wetting over the substrate, a role that is fundamentally related to the great number of functional groups present at the interface. In the case of hydroxyl-terminated dendritic PAMAM (G_n-OH) (Essawy *et al*. 2010), enhanced stability of the modified UF resin along with remarkable reduced levels of free formaldehyde and improved mechanical performance of wood joints were obtained.

As is well known, dendrimers are costly and laborious to obtain because of the numerous protection, deprotection, and purification steps during the preparation process. In contrast, hyperbranched polymers, which have a similar chemical structure to dendrimers, can be prepared by one-pot polymerization of an AB_n type monomer (Kim 1992). As the hyperbranched polymers can be attained in a much simpler way and much cheaper price, they are more practical and suitable for the modification of UF resins (Mamiński *et al*. 2007, 2009).

In a previous study (Amirou *et al*. 2014), a series of water-soluble aliphatic hyperbranched PAMAMs synthesized by one-pot polymerization according to the literature (Liu *et al*. 2005), namely, HB(MA-EDA)1, HB(MA-EDA)3, and HB(MA-DETA)1.2, were successfully utilized to upgrade the performance of melamine-urea-formaldehyde (MUF) resins. This could be attributed to the high reactivity of this class of polymers as a result of the high number of terminal reactive functional groups. It was hypothesized that the addition of PAMAMs to UF resin would also affect and enhance the mechanical properties of particleboards. Thus, the present study was conducted to investigate the effect of hyperbranched PAMAMs on the performance of UF resins.

EXPERIMENTAL

Materials

Urea and methanol were purchased from Merck-Stutgart OHG (Germany). Formaldehyde, methyl acrylate (MA), ethylenediamine (EDA), and diethylenetriamine (DETA) were provided by Sigma-Aldrich (France). All other chemicals were of laboratory grade and used without further purification. An industrial mixture of core particles of beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*), with moisture contents around 4%, was used for particleboard production.

Methods

Synthesis and characterizations of hyperbranched poly(amidoamine)s

Ethylenediamine was reacted with MA in different molar ratios (Liu *et al*. 2005). Ethylenediamine (18.03 g, 0.3 mol) and methanol (28 mL) were added to a one-neck flask. Then, MA (25.83 g, 0.3 mol) was added dropwise into the flask under continuous stirring at room temperature for about 2 days, after which the solvent was removed under vacuum. The reaction was then kept to progress for 1 h at 60 °C, 2 h at 100 °C, 2 h at 120 °C, and 2 h at 140 °C while applying high vacuum to obtain a viscous yellow product denoted as HB(MA-EDA) 1 in the first case. The process was repeated with a molar ratio of MA to EDA of 3:1 to obtain eventually HB(MA-EDA) 3 and a molar ratio of MA to DETA of 1.2:1 to get HB(MA-DETA) 1.2.

A Bruker AVANCE-400 spectrometer (Germany), with a CPMAS probe for 4 mm diameter rotors at a rotational speed of 12 kHz, was used for recording the Carbon 13 nuclear magnetic resonance (^{13}C-NMR) spectra of these polymers. The pulse duration at 90° was 3.9 ms, and the contact time was 1 ms (using cpramp100) with a recycle time of 5 s. Decoupling was used in CW mode. The chemical shifts of ^{13}C spectrum were reported in ppm relative to tetramethylsilane by taking the methine carbon of solid adamantane (29.50 ppm) as an external reference standard. Molecular weight determination of the polymers was performed on a Schambeck SFD SFD9425 Gel Permeation Chromatograph (GPC; Germany), with Agilent (USA) 1100 columns in series, equipped with a refractive index detector. N,N-Dimethylformamide (DMF) was employed as the solvent and polystyrene (PS) as the standard.

Preparation and characterization of modified UF resins

The UF resins were synthesized in the laboratory by a typical three-step procedure (alkaline-acidic-alkaline) as described previously (Zhang *et al*. 2013). In the cases of the modified UF resins, hyperbranched PAMAMs were added to the UF resin just before particleboard production in different proportions based on the solids content: 1, 3, 5, and 10%. Additionally, another modified UF resin was prepared by employing a solution of 20% HB(MA-EDA)1 instead of sodium hydroxide to adjust the pH during the whole synthesis.

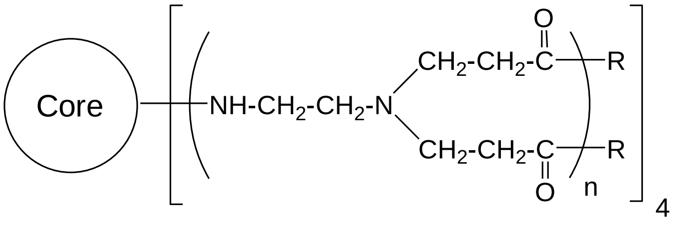
The gel time was noted as the time that elapsed until gelation occurred at 100 °C, after the addition of 1% ammonium chloride or formic acid as a curing agent (based on the resin weight). The curing reactions of the different resin systems were evaluated using a Mettler TMA SDTA 840 thermomechanical analyzer (Switzerland) with STARe software for data treatment. All experiments were conducted under the same conditions: 22 mg of resin was spread between two beech wood veneers of dimensions 17 mm × 5 mm × 0.5 mm. Each specimen was measured in three point flexion mode in the temperature range of 25 to 250 °C, with a heating rate of 10 °C/min. The cured resins were investigated using Fourier transform infra-red (FTIR) analysis in transmittance mode using a JASCO FTIR-6100E spectrometer (Japan). All the resins were initially cured and then soaked in water for 24 h while refreshing the water periodically, followed by complete drying before investigation.

Wood particleboards preparation and testing

Triplicates of one-layer particleboard with dimensions of 350 mm × 300 mm × 14 mm were pressed at 180 °C for 7.5 min under a maximum pressure of 3.3 MPa. The resin solids content was 10% based on dry wood particles. All particleboards were tested for internal bond (IB) strength, the modulus of rupture (MOR), the thickness swelling, and the water absorption as well as the formaldehyde emission. The IB strength was measured using an Instron 4467 universal testing machine (Instron Corp., USA) operated at a speed of 2 mm/min. The formaldehyde emission was tested according to European Standard EN 717-3 (1996).

RESULTS AND DISCUSSION

Three types of hyperbranched PAMAMs, namely HB(MA-EDA)1, HB(MA-EDA)3, and HB(MA-DETA)1.2, were prepared as in previous work (Amirou *et al.* 2014). The number after each structure refers to the feed ratio of its components. As a typical example, Fig. 1 depicts the general chemical structure of HB(MA-EDA)s regardless of the feed ratio of MA to EDA.



$\text{Core} = -[CH_2N(CH_2CH_2CO)_2]_2$

$\text{R} = -OCH_3$ or $-NHCH_2CH_2NH_2$

Fig. 1. General chemical structure of HB(MA-EDA)s

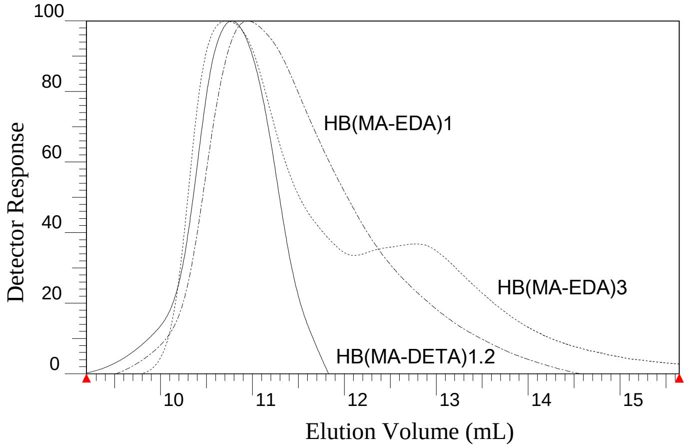


Fig. 2. GPC chromatogram profiles of the prepared hyperbranched polymers

The molecular weights of the prepared structures were determined by GPC (Fig. 2). The chromatograms ensure successful formation of the anticipated structures in polymeric forms as deduced from the assigned molecular weights in each case. The values of number-average molecular weight (M_n), weight-average molecular weight (M_w), z-average molecular weight (M_z), and polydispersity (M_w/M_n) are summarized in Table 1. The molecular weights of the HB(MA-EDA)s decreased with increasing the MA: EDA ratio from 1 to 3. Conversely, the polydispersity increased, indicating that the molecular weight distribution broadened with decreasing the EDA molecules in the reaction system; therefore, it is possible to prepare HB(MA-EDA)s of different molecular weights by varying the MA: EDA ratio.

Table 1. Molecular Weights and Polydispersity of the Hyperbranched Polymers

Hyperbranched Polymers	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	M_w/M_n
HB(MA-EDA)1	4.86×10^3	9.86×10^3	1.45×10^4	2.03
HB(MA-EDA)3	2.38×10^3	9.46×10^3	1.52×10^4	3.98
HB(MA-DETA)1.2	1.38×10^4	1.62×10^4	1.96×10^4	1.17

In addition, these hyperbranched polymers were characterized by ^{13}C-NMR (Fig. 3). The ^{13}C-NMR spectra of the three PAMAMs are generally characterized by peaks at 31 to 59 ppm ($\underline{C}H_2$, $\underline{C}H_3$) and 171 to 178 ppm ($\underline{C}$=O) (Liu *et al*. 2005). The peak strength of the methoxyl groups increased, while that of the primary and secondary amino groups decreased with the augment of the feed ratio of monomer molecules (MA) to core molecules (EDA or DETA). This indicates that with a larger molar ratio of MA to EDA or DETA, more methoxyl groups residual and less amine groups residual are present in the polymer. In other words, the hydrophobic character increased with the emergence of terminal methoxyl groups at the expense of some amino groups when the MA ratio increased with respect to EDA.

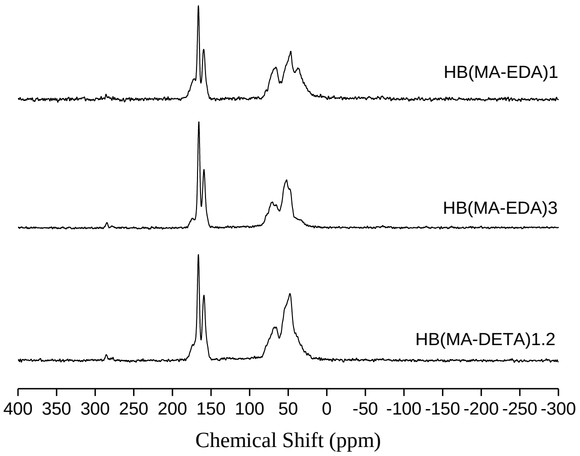


Fig. 3. The related ^{13}C-NMR spectra of these PAMAMs (Amirou *et al.* 2014)

When it comes to the application of PAMAMS as UF resin additives, the first concern is the difference in curing mechanisms between UF and MUF resins. The MUF resin can be cured under alkaline conditions, while the UF resin can only be cured under acidic conditions. In that case, even though all the PAMAMs, HB(MA-EDA)1, HB(MA-EDA)3, and HB(MA-DETA)1.2 were suitable for modifying MUF resin, they may not have the same positive effect on UF resin when intended only as additives, or better to say, not permanently attached to the UF network. The first concern is the high pH value of PAMAMs, in particular when terminated with amino groups. In the cases of HB(MA-EDA)1 and HB(MA-DETA)1.2, the pH values of their 20% solution were around 12 to

13, indicating that the strong alkalinity will cause a serious adverse effect on the curing of the UF resin. To be specific, the pH value of the UF resin increased from 8.36 to 10.25 with the addition of 3% HB(MA-EDA)1. For this reason, these two polymers were abandoned in this section. For HB(MA-EDA)3, which is much less basic due to the replacement of many amino groups with methoxyl terminals, the pH was around 8; thus it seems to be more suitable for the modification of UF resin. The HB(MA-EDA)3 was therefore added to the UF resin in different ratios based on the solids content, 1, 3, 5, and 10 %, and then the modified UF resins were used as particleboard binders. As expected, the pH values almost did not change after the addition of HB(MA-EDA)3 (Table 2). The thermomechanical behavior of the modified UF resins as well as the properties of particleboards bonded with these resins were investigated.

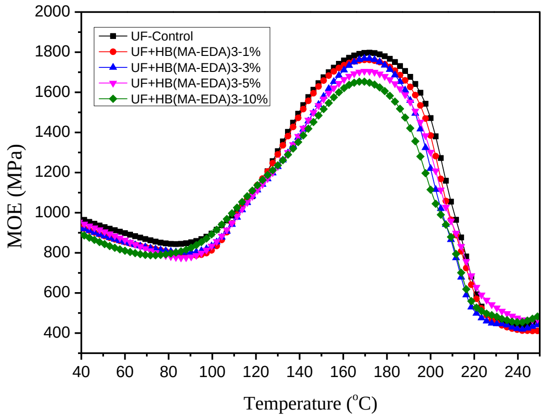


Fig. 4. TMA curves of the modified UF resins with different proportions of HB(MA-EDA)3

Table 2. Characteristics of Particleboards Prepared with the Modified UF Resins with Different Proportions of HB(MA-EDA)3 (Mean ± Standard Deviation)

Addition of HB(MA-EDA)3 (%)	pH	Density (g/cm^3)	IB (MPa)	MOR (MPa)	Formaldehyde emission (mg/100 g)	Thickness swelling (%)		Water absorption 24 h (%)
						2 h	24 h	
0	8.36	0.71±0.01	0.83±0.07	17.08±1.12	5.624±0.284	23.16±1.46	33.06±2.09	69.31±3.63
1	8.68	0.72±0.01	0.78±0.09	18.10±1.35	5.971±0.320	24.20±1.55	34.59±2.56	71.11±3.84
3	8.74	0.71±0.01	0.76±0.09	17.46±1.21	5.696±0.257	26.35±1.38	36.65±2.89	70.82±3.91
5	8.64	0.71±0.01	0.64±0.05	16.62±1.60	5.508±0.236	28.59±1.79	39.67±2.94	73.22±3.76
10	8.78	0.71±0.01	0.54±0.06	17.11±1.38	6.483±0.384	30.32±2.11	41.89±2.95	74.2±4.12

A thermomechanical study using thermomechanical analysis (TMA) was recorded on the prepared samples in order to explore the probable consequences of the addition of HB(MA-EDA)3 on the strength of the resulting modified networks. Figure 4 shows the related TMA profile in each case. Unlike the tendency in MUF resins (Amirou *et al.* 2014), the peak of modulus of elasticity (MOE) decreased with the insertion of the HB(MA-EDA)3. The higher the addition of HB(MA-EDA)3, the lower the obtained peak intensity of MOE. The continuous drop might be caused by the over-plasticization and the induced looseness of the network structures with the addition of HB(MA-EDA)3 (Zhou *et al*. 2013, 2014). Even though the MOE of the modified UF resins suggested a negative influence of HB(MA-EDA)3 on the end rigidity of the cured resins, the real effect of HB(MA-EDA)3 on the UF resin in the application of particleboard needed to be verified by the properties of the particleboards fabricated with these modified UF resins. Particleboards were therefore manufactured and tested as shown in Table 2 (1% NH_4Cl was used as a curing agent).

It can be observed that the IB strength of the formulated particleboard with pure UF resin was averaged at 0.83 MPa, and the IB strength decreased with increasing the proportion of HB(MA-EDA)3. Similar tendencies were found in the other properties, such as MOR, thickness swelling (both 2 h and 24 h), and water absorption. Moreover, the addition of HB(MA-EDA)3 had an irregular influence on the formaldehyde emission. In general, the addition of HB(MA-EDA)3 caused some adverse effects on the performance of the produced particleboards. This was in accordance with the tendency of the obtained maximum MOE values from the TMA curves, which can predict the end rigidity of the cured systems.

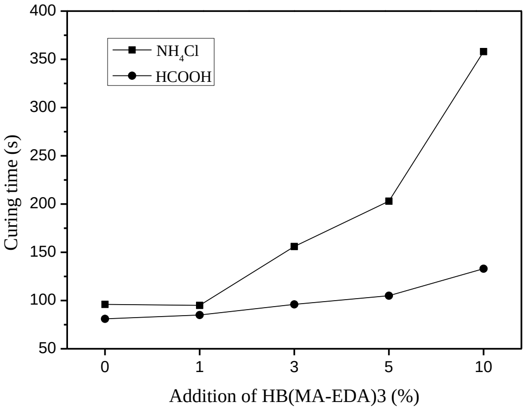


Fig. 5. Gel time of the modified UF resins with different curing agents

Gel time, which signifies the resin reactivity, was determined in all cases for predicting the impact of each modifier (Fig. 5). When 1 % NH_4Cl was used as the curing agent, the gel time was assigned as 96 s for the unmodified UF resin. It increased tremendously with the increment of HB(MA-EDA)3. The reason for this phenomena might be the high buffer capacity of the hyperbranched polymer, which was due to the basicity of the terminal amino groups from one side and the lesser reactivity of the methoxyl groups from another side. Consequently, the acid buffer capacity was measured in this study, which was defined as the millimole (mmol) of acid needed to titrate 10 g of resin (dissolved in 200 mL of distilled water) to pH 5.00 with a 0.05 N formic acid solution. The acid buffer capacity of the UF resin modified with 5% HB(MA-EDA)3 was 1.308 mmol, which is three times as high as that of the pure UF resin (0.434 mmol). Because acidic conditions are preferable for the curing reaction of a UF resin, high buffer capacity is not favorable for the UF resin curing. This might be the reason for the prolongation of gel time. The maximum gel time reached 360 s with 10% HB(MA-EDA)3, indicating that longer hot-pressing time or higher hot-pressing temperature are needed to cure the modified UF resins, which is detrimental to particleboard industrial production. Under the same hot-pressing parameters as the UF resin, the curing degree of the modified UF resins was lower than that of the UF resin, which accounted for the deterioration of the produced particleboard; therefore, another stronger curing agent, HCOOH, was used instead of NH_4Cl, and the gel time was measured. As expected, the gel time with 1% HCOOH as the curing agent was lower than the cases when NH_4Cl was used. In addition, the gel times with different proportions of HB(MA-EDA)3 were not noteworthy as compared to pure UF resin. Particleboards were manufactured with the modified UF resins by using 1% HCOOH as a curing agent. The performance of the particleboard was investigated and is displayed in Table 3.

Table 3. Characteristics of Particleboards Prepared with the Modified UF Resins with Different Proportions of HB(MA-EDA)3 (Mean ± Standard Deviation)

Addition of HB(MA-EDA)3 (%)	Density (g/cm^3)	IB (MPa)	MOR (MPa)	Formaldehyde emission (mg/100 g)	Thickness swelling (%)		Water absorption 24 h (%)
					2 h	24 h	
1	0.72±0.01	0.72±0.06	17.15±1.33	6.605±0.406	24.92±1.51	33.48±2.02	70.85±3.76
3	0.72±0.01	0.76±0.05	18.14±1.24	6.142±0.395	26.09±1.83	35.80±2.40	71.50±4.05
5	0.72±0.01	0.74±0.05	17.62±1.52	6.592±0.400	25.51±1.76	35.21±2.38	68.55±3.47

With the shortening of the gel time, the performance of particleboards did not show a continuous drop with the increase of HB(MA-EDA)3 as for the cases of NH_4Cl. The IB strength increased first and then declined slightly with the increase of HB(MA-EDA)3. The subsequent decline with additional loadings accounted for the over-plasticization caused by excessive amounts of the modifier (Amirou *et al.* 2014). The highest IB strength obtained was 0.76 MPa, which was to some extent lower than that of the pure UF resin (0.83 MPa). The formaldehyde emissions were expectedly higher than those in the cases of NH_4Cl, as it depends on the consumption of some free formaldehyde in its curing reaction. Additionally, the other properties of the particleboards bonded with the modified UF resins were lower than those in the case of the pure UF resin. In the end, this strong acid as a curing agent could not upgrade the performance of the produced particleboards. The possible reason might be the fact that wood particles were destroyed by the strong acid, which could have caused deterioration of the mechanical properties of the particleboard. In brief, this hyperbranched polymer, HB(MA-EDA)3, was not suitable for the modification of UF resins as particleboard binders, at least when it was added as a final additive. This may imply the necessity for starting the modification of UF resins with this modifier in the early steps of the resin preparation to ensure effective insertion into the network structure (Essawy *et al*. 2009; 2010; Essawy and Mohamed 2011).

Table 4. Characteristics of Particleboard Bonded by the Modified UF Resin with HB(MA-EDA)1 as a pH Regulator Instead of Sodium Hydroxide***** (Mean ± Standard Deviation)

Density (g/cm^3)	IB (MPa)	MOR (MPa)	Formaldehyde emission (mg/100 g)	Thickness swelling (%)		Water absorption 24 h (%)
				2 h	24 h	
0.72±0.01	0.92±0.07	16.87±1.46	5.431±0.269	21.68±1.29	29.83±1.97	68.40±3.56
*****1% NH_4Cl was used as a curing agent						

To enhance the water resistance of the MUF resin, these reactive PAMAMs were also used as additives to adjust the pH at the end stage instead of using sodium hydroxide, as in a previous study (Amirou *et al.* 2014). It was interesting to find that the modification at the end stage with only 0.08 wt% instead of sodium hydroxide resulted in better results than the pure MUF resin. Therefore, in this study, these hyperbranched PAMAMs were also utilized as pH regulators in place of sodium hydroxide during the synthesis of the UF resin. Concerning the differences of the pH value and the degree of branching, a 20% solution of HB(MA-EDA)1 was used to adjust the pH instead of sodium hydroxide during the whole resin synthesis. The total amount of the solid HB(MA-EDA)1 was around 0.72% based on the resin weight. Particleboard was prepared and evaluated to investigate the effect of this pH regulator on the performance of particleboard bonded with the modified UF resin (Table 4).

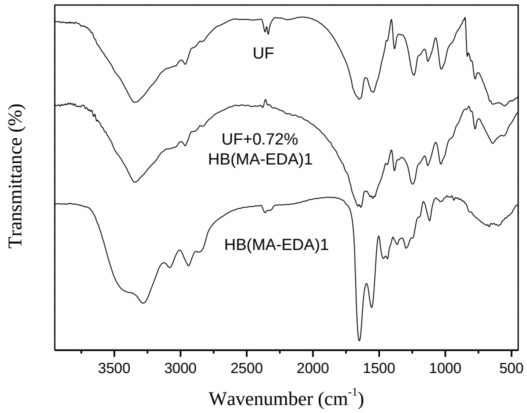


Fig. 6. FTIR spectra of the pure and modified UF resins as well as HB(MA-EDA)1

With a very finite incorporation of HB(MA-EDA)1 as a pH regulator, the IB strength increased from 0.83 MPa to 0.92 MPa, and the formaldehyde emission decreased from 5.624 mg/100 g to 5.431 mg/100 g. These results revealed that a small addition of HB(MA-EDA)1 was effective to upgrade the performance of the UF resin. This may be attributed to the insertion of reactive hyperbranched structures, whose reactive terminal groups should qualify them as co-condensing agents and network modifiers through polycondensation reactions taking place during the particleboard production. To evaluate the improvements, FTIR analysis was conducted to characterize the cured modified UF resins as shown in Fig. 6. The main assignments of the FTIR spectra can be referred to in a previous work (Amirou *et al.* 2014). Here, the focus was on the incorporation of HB(MA-EDA)1 into the cured network; however, tiny perturbations were observed, but there was no recognizable difference between the spectra of the pure UF resin and modified UF resin with 0.72 % HB(MA-EDA)1. This may be due to the finite incorporation of HB(MA-EDA)1, which is difficult to detect by FTIR, considering that the spectra of a system like UF resin is very rich with bands, which makes it very difficult to detect a real change caused by such a very finite amount.

CONCLUSIONS

1. Unlike the cases of modified MUF resins, these hyperbranched PAMAMs caused mostly adverse effects on UF resin, especially upon consequent application in particleboard fabrication. The high pH and acid buffer capacity of these PAMAMs had a severe negative influence on UF resin curing, which requires acidic conditions.

The gel time was prolonged tremendously, and the maximum MOE values obtained from TMA curves decreased with the addition of HB(MA-EDA)3. The use of formic acid as a curing agent could reduce the gel time; however the performance of the particleboards still deteriorated. Therefore, these hyperbranched PAMAMs are not suitable for the modification of UF resin, at least when employed as final additives.

2. The modified UF resin with employing 0.72% HB(MA-EDA)1 for pH adjustment instead of sodium hydroxide yielded a considerable upgrade of the performance of the produced particleboard. The noticeable improvements, however, need to be further investigated in the future.

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