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RESEARCH ARTICLE

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Adhesive application method in MDI-UF particleboard manufacture

Abstract Chinese wood-based composite manufacturers are plagued with serious formaldehyde emission (F-emission) problems. In this study, we investigated the use of an emulsifiable diphenylmethane-4, 4'-diisocyanate (MDI) – urea formaldehyde (UF) mixture adhesive in particleboard manufacture, in order to decrease F-emission to below 9 mg per 100 g board. We paid close attention to the effect of NH_4Cl on MDI-UF curing and the method of adhesive application by differential scanning calorimetric (DSC) analysis and compared mechanical properties. Both results showed that the acidic agent NH_4Cl did hinder EMDI-UF curing and it also affected the adhesive application method. We are of the opinion that when EMDI and UF are mixed first, without adding NH_4Cl and then sprayed onto particles, mechanical properties will be improved and F-emissions will meet E1 grade requirements.

Keywords UF-MDI adhesive mixture, formaldehyde emission, particleboard, curing agent, separate application, mixing application

1 Introduction

People have tried to mix MDI with traditional wood industry adhesives for decades in order to decrease cost or to improve mechanical properties (Tinkelenberg et al., 1982; Pizzi and Walton, 1992; Hao and Liu, 1993a, 1993b; Pizzi et al., 1993; Deppe, 1997; Grigoriou, 2000; Frick and Motter, 2001; Simon et al., 2002). However, spray application of UF and/or MDI adhesives to wood particles remained a bone of contention.

Pizzi (1983) mentioned that when MDI and amino-resin are applied separately, both internal bond strengths of dry and wet boards are maintained. However, when the two adhesives were mixed and then sprayed, the board's internal bonding strength was reduced to only 30%–50% of its original strength. In another study on manufacturing exterior plywood, Pizzi (1993) used a normal amount of ammonium chloride (NH_4Cl) as a hardener for the UF portion of the resin mixture. The glue mixture was assembled by adding MDI to the UF resin, mixing and subsequently adding other components, including NH_4Cl. The mixed MDI-UF adhesive systems showed a remarkably good performance.

Hao and Liu (1993b) found that rather than adding a hardener, spraying the EMDI-UF mixture without adding NH_4Cl gave the best results. Tinkelenberg et al. (1982) asserted that the isocyanate group (–NCO) is capable of reacting with active hydrogen in almost any form under either acid or alkaline conditions. In their experiment, they added NH_4Cl to glue solutions and compared the mixed application with the separate application. Differences in the procedure of application hardly existed.

Little is understood about which spray method works best (i.e., mixing the MDI and UF and then spraying, or separately spraying each of the components). The objective of this study was to discuss the impact of an acidic hardener on the reaction of UF with MDI and to develop an optimum method of mixture adhesive application. The products should adhere to the Chinese National Particleboard Standard GB 4897-92 requirements for mechanical and physical properties and the E1 requirement for formaldehyde emission (F-emission).

2 Materials and methods

The materials we used were the same as those mentioned before (Wang et al., 2004). For our experiment, Dow Chemical Company donated the emulsifiable MDI adhesive. The MDI had been chemically modified and could be dispersed directly into aqueous emulsion glues. The functionality was 2.7, and –NCO content was 30.1%. The

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UF resin (U/F molar ratio 1:3) was purchased from a particleboard plant; its solid content was 64% and its pH 7.8. The UF was catalyzed by an NH_4Cl solution of 25% content. Wax (50% content) used as water repellent, was applied at a ratio of 0.7% of oven-dry weight of the particles. The wood particles consisted of mainly poplars, mixed with some birch.

MDI and UF were mixed or separately sprayed onto particles. In the mixed application, MDI was first added to a UF resin solution. After it was uniformly mixed, the mixture was sprayed onto particles. In a separate application, UF was sprayed onto particles first and then MDI was applied with a spray. Based on the oven-dry weight of particles, 6% UF resin and 1% MDI were used in both mixture spray and separate sprays. NH_4Cl was considered a variable: it was either added or not added. The particle/adhesive mixture was manually formed into a mat of 320 mm×330 mm. The mat of 14%–16% moisture content was then hot-pressed at 175°C for 6 min into a 12-mm-thick particleboard. Each combination condition was replicated six times. In accordance with the Chinese National Particleboard Standard GB4897–92, the resulting particleboards were tested for modulus of rupture (MOR), modulus of elasticity (MOE), internal bond strength (IB) and thickness swelling (TS) (listed in Table 1).

DSC was performed on samples at a rate of 10 ºC/min. Both the temperature and reaction-heats were obtained by integrating endothermic peak areas and are reported in Table 2.

3 Results and discussion

When NH_4Cl was added as a curing agent and the MDI and UF were sprayed separately, the board properties were better than when the sprays were mixed. MOR, MOE, TS and IB improved 12.7%, 17.7%, 15.2% and 25%, respectively. When NH_4Cl was not added, the properties of boards sprayed with the mixed spray were better than those sprayed separately (Table 1). MOR, MOE, TS and IB improved 19.4%, 5.8%, 32.8% and 25.8%, where TS and IB improved significantly. There were no statistically significant differences between the mechanical properties of particleboard made with the mixed spray without NH_4Cl and those made with the separately applied sprays and added NH_4Cl (t-test: p-value = 0.261). However, we have to consider their differences in F-emission.

Table 1 The properties of UF/MDI particleboard pressed at 175ºC for 6 min

NH_4Cl	Spray methods	Density /(g·cm^{-3})	MOR /MPa	MOE /GPa	TS /%	IB /MPa
Yes	Mixed	0.61 (0.020)	13.49 (2.754)	1.98 (0.347)	6.05 (1.147)	0.28 (0.053)
Yes	Separate	0.61 (0.020)	15.20 (2.27)	2.33 (0.292)	5.13 (0.771)	0.35 (0.065)
No	Mixed	0.63 (0.018)	16.21 (4.070)	2.36 (0.404)	4.31 (1.918)	0.39 (0.099)
No	Separate	0.64 (0.019)	13.58 (2.393)	2.23 (0.254)	6.41 (1.308)	0.31 (0.079)

The mechanism of UF curing begins with the addition of acid or acidic salt, which can be released during hot-press to decrease the pH and to accelerate the condensation reaction. On the other hand, MDI is cured at a neutral pH. Acid is often used as a stabilizer to neutralize basic substances in the reaction, inhibit side reactions and forestall pre-polymer jellification (Shanxi Province Chemical Industry Institute, 2001). In particleboard manufacturing, sprayed adhesive is dispersed on particle surfaces as droplets. When UF and MDI were sprayed separately, the UF could not ensure a complete reaction with MDI because a small portion of UF was in contact with MDI. The residual non-reacted UF without NH_4Cl was in a neutral or weak basic state, which slowed down its condensation rate and lessened cross-linkages, leading to poor bonding strength. When the two adhesives were sprayed as a mixture, the UF and MDI were mixed uniformly. So it was possible for the MDI, as a reaction medium, to react chemically with both the wood and the UF, forming stable bond connections and thus reinforcing strength.

The method of adhesive application onto particles is closely related to adding or not adding NH_4Cl. The acidic hardener of UF retards MDI curing. Ranking all the properties, the adhesive application method should be as follows: mix UF/MDI then spray without NH_4Cl > spray separately with NH_4Cl > spray separately without NH_4Cl = mix UF/MDI with NH_4Cl then spray.

Emulsifiable MDI can safely mix with UF and make it possible to use the MDI/UF mixture in industrial applications. We also tested the stability of the UF/MDI mixture. After the UF/MDI mixed adhesive was sprayed, glued particles stayed 2 h and were then pressed into the board. The properties of these boards did not significantly differ from those of immediately pressed boards. However, it was found that the viscosity of the mixture increased considerably over time, which made the spray operation difficult. In practical applications, it is better to mix UF and MDI together just before spraying.

Results of DSC are listed in Table 2 and are shown in Figs. 1–4. Figure 1 reveals that MDI did not self-polymerize at less than 260ºC; it eventually decomposed at higher temperatures. This indicates that heat of endothermic reaction in Figs. 3 and 4 results from UF polymerization or the reaction between UF and MDI. Figures 2 and 3 compare the DSC of UF adding and not adding MDI. When NH_4Cl was added to the UF/MDI mixture system, there were no significant differences between the two graphs; the starting temperature, point temperature and duration are similar. Based on the ratio of UF to MDI (6:1), the calculated endothermic heat of UF in the mixture is 199 J/g, which is the same with that of pure UF curing. When NH_4Cl was added, UF totally cured using its original mechanism, without being reinforced by the MDI.

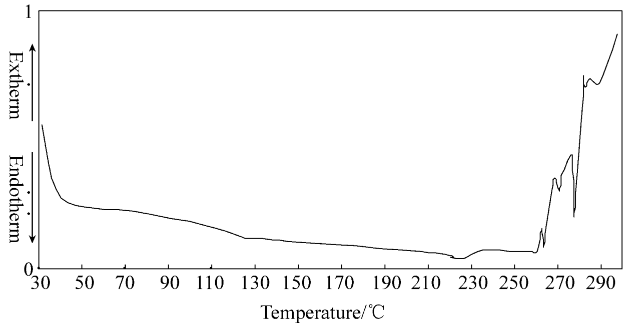


Fig. 1 DSC of MDI

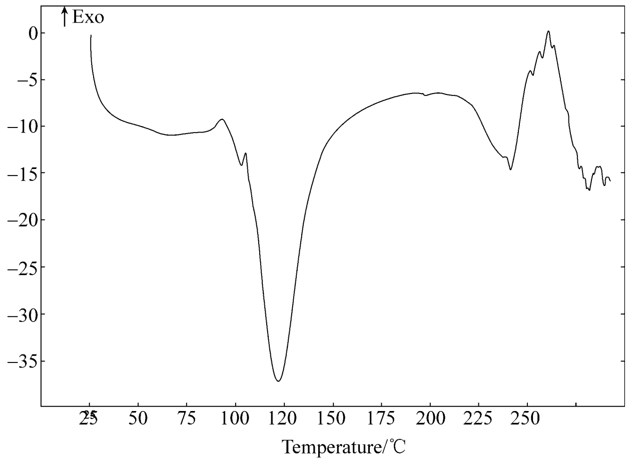


Fig. 2 DSC of UF curing with NH_4Cl

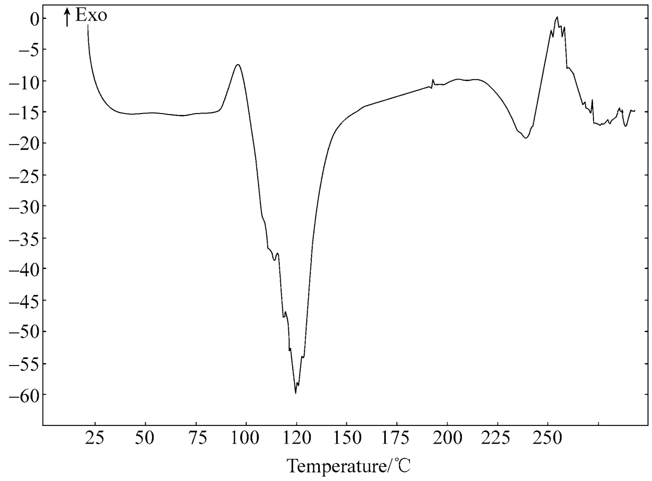


Fig. 3 DSC of UF-MDI mixture curing with NH_4Cl

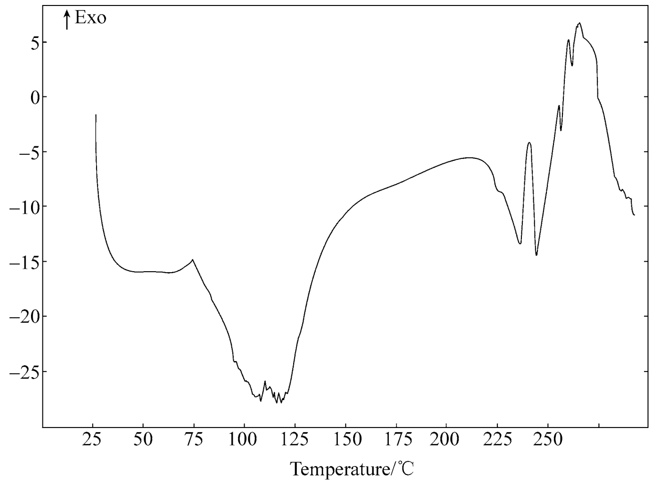


Fig. 4 DSC of UF-MDI mixture curing without NH_4Cl

Table 2 Endothermic parameters of different adhesives

Adhesive	Endothermic starting temperature /ºC	Endothermic peak point temperature /ºC	Endothermic energy /$(J\cdot g^{-1})$
UF + NH_4Cl	107.09	122.06	200.24
UF+ MDI	86.18	118.51	127.25
UF+ MDI + NH_4Cl	111.96	124.81	170.59

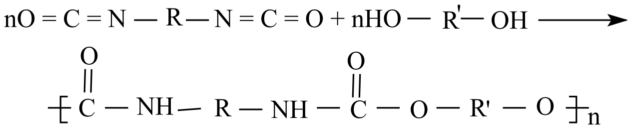
When NH_4Cl was not added, Fig. 4 shows that the endothermic peak of UF/MDI mixture starts at 86 ºC, much lower than that of Fig. 3. Given the ratio of 6:1, endothermic heat of UF is calculated as 148 J/g. This means UF required less energy when it reacted with MDI at a lower temperature, than when UF condensed and UF-MDI cured under acidic conditions. UF reacted with MDI well when NH_4Cl was not added to the mixture.

The physical and mechanical properties of particleboard improved when the UF/MDI mixture adhesive was sprayed without NH_4Cl; the reason for this is not the overlay impact of UF curing plus MDI curing. The reaction may exist between UF and MDI, forming stable chemical bonds. We hold that co-polymerization between UF and MDI led to the good qualities in the particleboard made with the mixed spray.

For the boards where the adhesives were applied separately with the addition of NH4Cl, the better qualities mainly resulted from the condensation of UF, plus MDI reacting with the wood. In this case, there were still some unstable bonds such as those formed in pure UF particleboard, which had the potential for releasing formaldehyde.

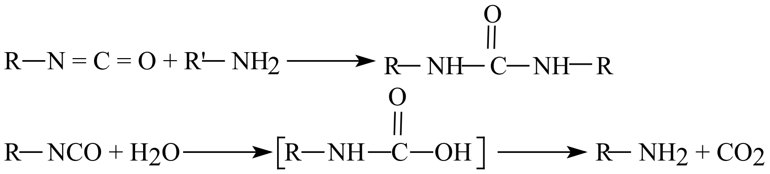
In the condensation reaction of UF resin, methylolureas formed big molecules, containing a lot of active end groups such as hydroxymethyl (–CH_2OH). In the case of MDI, its main reaction is with the hydrogen atom of compounds. The possible reactions existing in the UF/MDI mixture system are listed as follows:

The reaction of MDI with hydroxide:



$$nO=C=N-R-N=C=O + nHO-R'-OH \longrightarrow \left[\overset{O}{\overset{\|}{C}}-NH-R-NH-\overset{O}{\overset{\|}{C}}-O-R'-O \right]_n$$

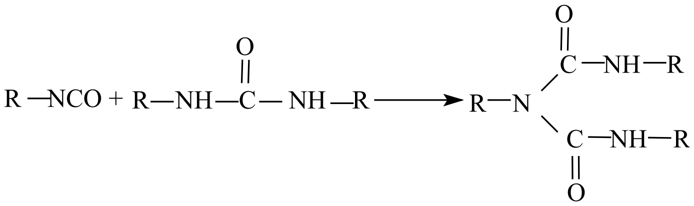
The reaction of MDI with amide:



$$R-N=C=O + R'-NH_2 \longrightarrow R-NH-\overset{O}{\overset{\|}{C}}-NH-R$$

$$R-NCO + H_2O \longrightarrow \left[R-NH-\overset{O}{\overset{\|}{C}}-OH\right] \longrightarrow R-NH_2 + CO_2$$

The reaction of MDI with carbamide:



$$R-NCO + R-NH-\overset{O}{\overset{\|}{C}}-NH-R \longrightarrow R-N(C(=O)-NH-R)_2$$

Pizzi (1993) revealed that one main mechanism for co-polymerizing UF and MDI is based on the reaction of the –NCO group of the isocyanate with the active –CH_2OH group of UF. The second is the reaction of –CH_2OH with the activated aromatic ring of MDI. The relative reaction activity of functional groups under different environments is more complicated because of the introduction of wood and water into the mixed system. Continuing research on the real mechanism of bonding among UF, MDI and wood is needed.

In our study, both the results of DSC and the physical and mechanical properties of the particleboard showed that NH_4Cl retards the curing of the UF/MDI mixture system. The reaction of UF with MDI, without NH_4Cl, can avoid the potential decomposition of bonds such as F-emission formed during pure UF resin curing. Another test (Wang et al., 2004) has shown that, when pressed at 175ºC for 4.5 min, the F-emission was less than 8 mg per 100 g particleboard, which adheres to the Chinese national standard. Other physical and mechanical properties are also listed in Table 3 for comparison with pure UF bonding particleboard.

Table 3 The properties of particleboard pressed at 175°C for 4.5 min

Adhesive	NH_4Cl	Spray methods	Density /(g·cm^{-3})	MOR /MPa	MOE /GPa	TS /%	IB /MPa	F-emission /(mg/100g)
UF:MDI=6:1	Yes	Mixed	0.70 (0.017)	22.16 (3.350)	3.22 (0.647)	5.59 (1.424)	0.75 (0.150)	7.88
UF	Yes		0.71	23.22	3.17	6.01	0.70	36.77

4 Conclusions

Commercial UF could be used to manufacture a UF-MDI adhesive particleboard, leading to low F-emissions that meet E1 grade requirements, along with physical and mechanical properties that meet GB4897-92 requirements. This study has shown that acidic NH_4Cl inhibits the reaction of MDI with UF, affecting the adhesive application method. Adhesive application method should be in the following order: mix UF/MDI then spray without NH_4Cl > spray separately with NH_4Cl > spray separately without NH_4Cl = mix UF/MDI with NH_4Cl then spray. DSC also revealed that UF could react well with MDI in a mixture without NH_4Cl.

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