A COMBINATION OF POLYETHYLENIMINE AND PHENOLIC RESIN AS AN ADHESIVE FOR WOOD-BASED PANELS

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The purpose of this study is to develop a low-formaldehyde-emitting resin system for medium density fibreboards (MDF). A combination of polyamines with phenolic resins seems to be suitable for this purpose. To produce panels with such a resin system, polyethylenimine, and a phenolic resin were separately applied on fibres and subsequently made into boards in a thermal pressing process. It was demonstrated that thickness swelling and the mechanical properties of the boards produced with the new adhesive system were comparable to those conventionally manufactured with urea-formaldehyde resins. Even with adhesive contents of just 2 to 3%, the panels attained satisfactory internal bond strength. MDF panels with a total adhesive content of between 1.25 and 5% were produced from a mixture of polyethylenimine and phenolic resins (resol type) at different ratios. All boards were tested for physical (thickness swelling and water absorption) and mechanical properties (internal bond, modulus of elasticity, flexural strength). It was demonstrated that thickness swelling and the mechanical properties of the boards produced can be improved by a combination of polyethylenimine and phenolic resin.

Keywords: Novel adhesives; Phenolic resin; Adhesive for wood

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INTRODUCTION

Wood-based composites, especially MDF, are predominantly produced from wood as a natural resource. Additionally 8 to 12% of a synthetic resin is needed in a conventional production process to achieve sufficient bonding and high strength. Up to now, mostly urea formaldehyde resins (UF) have been applied in MDF production. The advantages of UF resins used as an adhesive for wood based panels are their high reactivity and their favourable prices. The high amounts of resin required, as well as the emission of formaldehyde during curing and furthermore from the manufactured product, are considerable disadvantages of these resins. Increasing ecological and health awareness has aroused interest in low-emission adhesives with a positive eco-profile. Thus the application of formaldehyde-free adhesives is a crucial competitive advantage for panel producers.

Polyamines such as polyethylenimine (PEI) and polyvinylamine (PVAm) are mainly used for increasing the dry and wet strength of paper and as retention and dehydration agents in the papermaking process. An advantage of these materials is that they are environmentally friendly. Unlike other types of substances, these bonding agents for wet paper contain no organically bound chlorine or formaldehyde (Stange and Auhorn 1999). The polyethylenimine molecule has a highly branched molecule structure. It contains primary, secondary and tertiary amino groups in amounts of 30%, 40%, and 30%, respectively (Fig. 1).

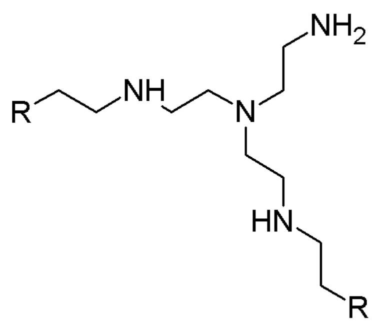


Fig. 1. Representational structure of polyethylenimine

As polyamines are easy and safe to handle, they can be used as an alternative adhesive for wood-based panels. Due to its availability, PEI has proven to be most suitable for the production of fibre boards. The ability of polyethylenimine to form hydrogen bonds is an important factor in its use as an adhesive. This effect derives from the high concentration of nitrogen-bound hydrogen atoms within the molecule (Espy 1995). Due to the high reactivity of the primary amino groups, PEI can interact with the carboxyl group containing components in acid-base reactions (Stange and Auhorn 1999). Other possible reactants for crosslinking reactions of the primary amino groups are epoxies, aminoplasts, isocyanates, anhydrides, aldehydes, and Michael acceptors. Besides formaldehyde and glyoxal reducing sugars (e.g. glucose), the reducing end of cellulose can serve as an aldehydic reactant for crosslinking reactions of PEI (Pinschmidt et al. 1996). The results of Fabo (2004) showed that the bonding mechanisms between PEI and fibers are based on a combination of mechanical interlocking, diffusion, adsorption, and covalent bonds. It was additionally shown that PEI and glucose react with each other to a high extent.

In various studies it could be demonstrated that it is possible to produce MDF with polyethylenimine as an adhesive. By comparison of PEI with a conventional UF resin it was shown that panels glued with PEI reached comparable internal bond strength at much lower adhesive contents; however, the values of thickness swelling were a little higher Also panels can be obtained even at high fiber moisture contents of up to 20% (Janneck 1999; Fabo 2004, Gu 2010).

Another approach to using PEI as an adhesive for wood-based panels is presented by Biedermann et al. (2001). The authors described a process for producing fibreboard panels by gluing fibres with an aqueous solution comprising a mixture of a polyamine (PEI or PVAm) and an amino resin (urea- or melamine-formaldehyde). Ebewele et al. (1991) also modified urea-formaldeyde resins with polyamines and showed that these had lower formaldehyde liberation than those cured with ammonium chloride.

For a combination of PEI with phenolic resins the reactivity of PEI with phenolic hydroxyl groups is of particular importance. Nimz et al. (1976) reported on crosslinking of sulphite spent liquors with PEI. Together with PEI, the spent liquors reacted under acidic conditions (pH 4.5) within a few minutes to form an insoluble resin.

Another approach to use the reactivity of PEI with phenolic hydroxyl groups is a combination of PEI with vegetable polyphenols (tannins). The mixture of the two components serves as a basis for a formaldehyde-free adhesive, which leads to high shear strength and shows considerable moisture resistance (Li et al. 2004).

Geng and Li (2006) investigated a wood-adhesive system consisting of kraft lignin and PEI for making two-ply plywood. The wood composites bonded with the lignin-PEI adhesive retained very high shear strength after undergoing a water soaking and drying test, as well as a boiling water test.

Phenol formaldehyde (PF) resins show a very high resistance of the C-C-bonding between the aromatic nucleus and the methylol group or the methylene bridge and therefore are used for water- and weather-resistant glue lines. They are principally used in the manufacture of plywood and oriented strand board (OSB). Another advantage of phenolic resins is the very low subsequent formaldehyde emission also due to the strong C-C-bonding (Dunky 2002).

Due to reactive sites (phenolic hydroxyl groups, hydroxymethyl groups and formaldehyde), as well as their low formaldehyde emissions, phenolic resins seem particularly suitable for a combination with polyethylenimine to form an adhesive for wood-based panels with low formaldehyde emissions.

In this study adhesive systems consisting of a phenolic resin (resol type) and polyethylenimine (PEI) were evaluated for bonding medium density fibre boards (MDF, interior type), and compared to panels produced with a conventional UF resin. As in the industrial process the resin is applied onto the fibres through different nozzles in the so-called blow line between defibration and drying, it seems to be easy to apply an additional resin component in this stage of the manufacturing process.

> The first hypothesis to be proven is that the panels bonded with a combination of PEI and a phenolic resin attain the same or better properties than the reference with much lower adhesive contents. With this hypothesis it should be proven whether the combined usage of PEI and a phenolic resin would be competitive to a standard adhesive with lower resin content. If this hypothesis holds, then it makes sense to consider this possibility in the future.

> The second hypothesis is that there is an interdependency of the relation and amount of the two components (PEI and PF). This hypothesis concerns the combined usage of the two resins types. The question is, whether the influence of PEI is independent of the load with PF resin, or whether the two resin contents influence each other according to certain panel properties. If this hypothesis is answered positively, the mixture of these resins should be considered, where the positive effect on the properties is still high and the necessary increase of resin content is as low as necessary

EXPERIMENTAL

The glue-free fibres for the production of Laboratory MDF were provided by Fundermax (St. Veit a. d.Glan, Austria) and air dried at room temperature to a moisture content of 7%. Beside the polyethylenimine (BASF, Lupasol G100), a resol phenolic resin was used. The resol type (Prefere 11J253) came from Dynea Erkner, Germany. The UF resin (Prefere 10F101) as the reference adhesive was supplied by Dynea Krems, Austria. The fibres were mixed with PEI in a batch mixer (EMT, WBH 75) equipped with ploughshares and inclined blade-type shovel tools as mixing tools to obtain an even distribution of the resin on the fibres. Subsequently the resol resin was also added into the mixer via a two-component jet. The amount of the adhesive components was varied between 0 and 2.5 % solid content respectively. Table 1 gives an overview of the options realised.

Table 1. Resin Loadings Realized in the Experiments

		PF (Resol)		
		0 %	1.25 %	2.5 %
	0 %		x	x
PEI	1.25 %	x	x	x
	2.5 %	x	x	x

The UF bonded reference panels were manufactured with a 10% resin loading. The blended fibres were formed into mats in a forming box, producing a random fibre orientation. The mats were pressed with a pressing rate of 2.8 N/mm^2 into boards for 2 minutes at 185°C. Each board had a size of 6x45x45 mm^2 and a density of 0.75 g/cm^3. Three panels for each option were produced. Mechanical testing of the fibre board materials was carried out by determining flexural strength by the three point method (EN 310) on 12 specimens of each option and internal bond strength EN 319 on 24 specimens of each option using a universal testing machine (Zwick Roll). The 24 h thickness swelling after immersion in water was measured according to the European Standard EN 317. The test was carried out on at least 24 specimens of each resin formation. All samples were conditioned at 65% relative humidity (RH) at 20°C before testing. Formaldehyde content was determined according to EN120.

Hypothesis 1:

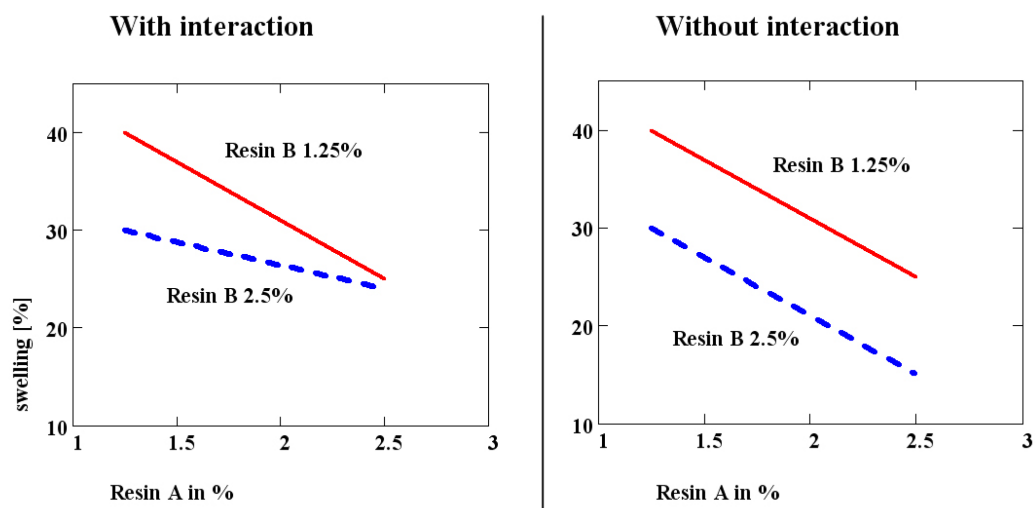
To test Hypothesis 1 the swelling and strength properties reached for the 10% UF resin loaded samples and the 2.5% PEI and 2.5% resol loaded samples were compared in a T-test. This test uses the standard deviation for the properties observed, and the sample groups are compared by their mean values.

Hypothesis 2:

To test the second hypothesis an analysis of variance (ANOVA) was applied. As there were two influencing factors (the content of PEI and PF resin), a two-way ANOVA was applied. Therefore the variation of the panel properties (swelling, internal bond strength and bending strength) was separated into the following four parts:

> the variation caused by the PEI content
> the variation caused by the PF content
> the variation caused by the interaction between those two contents
> the variation due to stochastic noise

The principle influence of an interaction is shown in Fig. 2.



With interaction

Swelling [%]		Resin B 1.25 %	Resin B 2.5 %
Resin A	1.25%	40	25
Resin A	2.5%	30	24

Without interaction

Swelling [%]		Resin B 1.25 %	Resin B 2.5 %
Resin A	1.25%	40	25
Resin A	2.5%	30	15

Fig. 2. Principle of an interaction between resin A and B according to the swelling behaviour

In Fig. 2 on the left side the influence of two factors (resin A and B) on a continuous property (swelling) is shown schematically by theoretical figures (see table below the graphs). The graph can be understood in the following way: If there is an interaction, the reduction of swelling by applying more resin A (increase in direction of the abscissa) is different depending on the content of resin B (left part of Fig. 2). If there is no interaction, the application of more resin A is leading to the same reduction of swelling independent on the content of resin B (right part of Fig. 2). It is important to determine whether there is an interaction or not, as many modeling approaches for material properties (e.g. multiple linear regression) assume independency between the variables.

To answer the question of whether there is an interaction between the PEI content and the PF resin content, the relevant test statistic (Hartung et al. 2005) was calculated and compared to the value of the F- distribution. All statistical analyses were performed with the software SPSS 14.0.

RESULTS AND DISCUSSION

Hypothesis 1

The hypothesis was tested with respect to thickness swelling, internal bond strength, and flexural strength. Samples containing 10% UF resin were compared with two PEI/Resol mixtures with a total adhesive amount of 3.75% (1.25% PEI and 2.5% PF) and 5% (2.5% PEI and 2.5% PF). The results are plotted in Table 2. At a total adhesive content of 3.75%, the thickness swelling of the boards bonded with PEI/PF mixture reached the level of the boards bonded with 10% UF. Statistically no significant difference could be ascertained. With a total adhesive content of 5%, the thickness swelling of the PEI/PF mixture bonded panels were significantly better than those of the UF reference. The average thickness swelling for 6 mm panels metioned in EN 317 is 19%. The higher values in this study is due to the fact that no hydrophobizing was used.

Table 2 also shows the comparison of the internal bond strength (IB). As well as the 5% option, the 3.75% option of the PEI/PF bonded panels reached significantly higher IB values than the UF reference.

Table 2. Thickness Swelling, Internal Bond Strength and Flexural Strength of Panels Bonded with PEI/PF Mixtures and UF Resin

	Thickness swelling [%]		Internal bond strength [N/mm]		Flexural strength [N/mm]	
	mean	sd	mean	sd	mean	sd
1.25% PEI + 2.5% PF	27.7	2.85	1.2	0.17	39.6	4.95
2.5% PEI + 2.5% PF	25.7	1.03	1.5	0.23	41.6	4.26
10% UF	28.9	2.56	0.8	0.10	42.8	3.6

By comparing the flexural strength values (Table 2) the PEI/PF mixtures showed the same level at considerable lower adhesive contents than the UF reference panel. These results indicate that with PEI/PF mixtures it is possible to produce panels with the same or even better properties at much lower adhesive contents. So it is demonstrated that the assumption of hypothesis 1 was correct. Table 3 gives an overview of the results described above.

Table 3. Results of the Hypothesis 1 Tests

	Thickness swelling	Internal bond strength	Bending strength
1.25% PEI + 2.5% PF	o	+	o
2.5% PEI + 2.5% PF	+	+	o

o = no significant difference to the UF reference

+ = significant better than the UF reference

Hypothesis 2

As in the case of hypothesis 1, hypothesis 2 likewise was tested with respect to thickness swelling, internal bond strength, and flexural strength. The ratio of the adhesive components (PEI and PF) was therefore varied between 0, 1.25 and 2.5%. In terms of the results of thickness swelling, the ANOVA showed a significant interdependency between the two adhesive components. This is shown in Fig. 3.

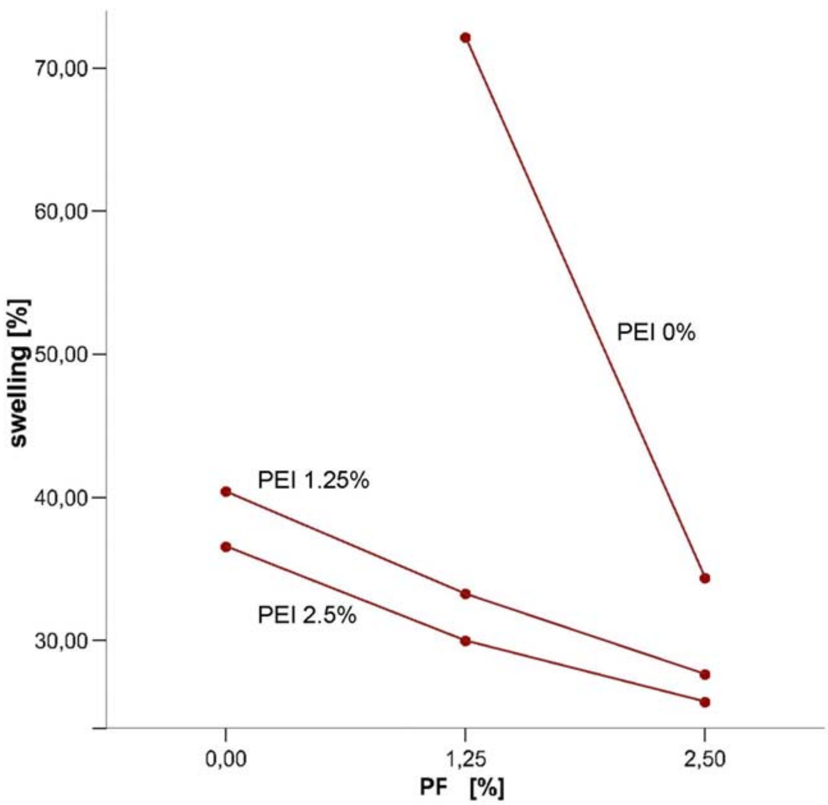


Fig. 3. Thickness swelling of fibre boards with different adhesive content

At an adhesive content of 1.25% the PEI bonded boards reached better (lower) values than the boards bonded with 1.25% PF. At a level of 2.5% there was no difference between the two resin types. By the application of 1.25% PEI, the swelling can be improved considerably. This effect decreases with an increasing amount of PEI, to 2.5%. The curves of equal adhesive contents (PEI+PF) became flatter with an increasing PEI ratio.

Figure 4 shows the results of the internal bond (IB) strength tests. The purely PEI bonded boards reached higher internal bond strength at 1.25% as well as at 2.5% in comparison with the purely PF bonded boards. In combination with PF, an increasing PEI content also leads to increasing IB values. But as already shown for the thickness swelling, the effect was lessened with an increasing PEI ratio. The interdependency of the adhesive components was also significant for the internal bond strength.

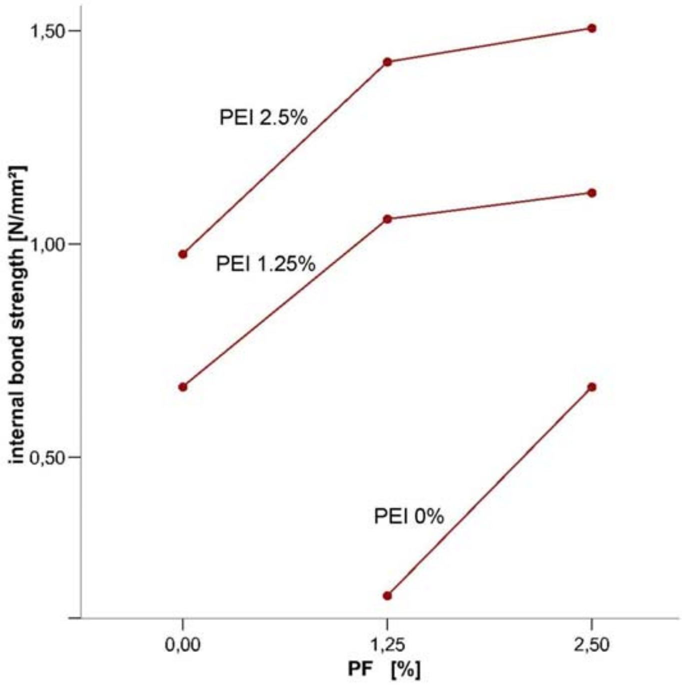


Fig. 4. Internal bond strength of fibre boards with different adhesive content

Figure 5 shows the impact of the adhesive content and the ratio of the two components on flexural strength.

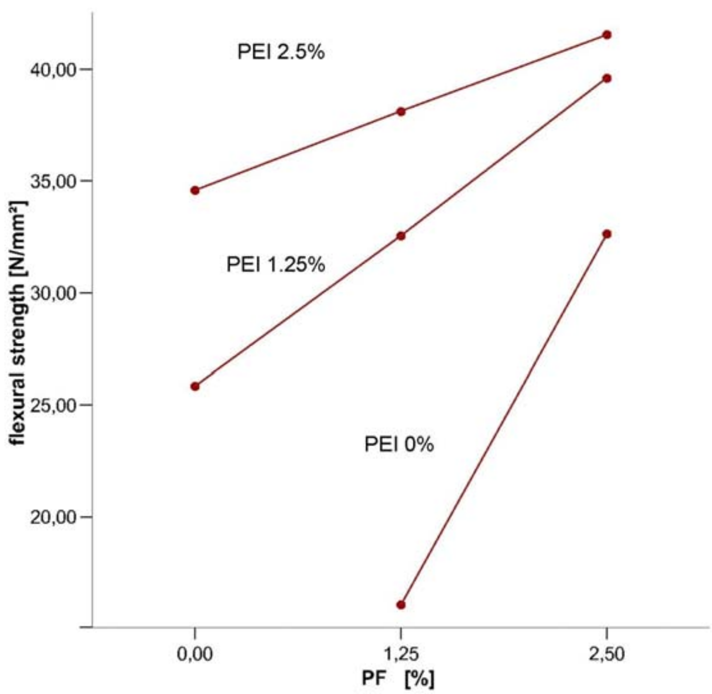


Fig. 5. Flexural strength of fibre boards with different adhesive content

As indicated here, the flexural strength of the panels increased with an increasing PEI amount. As in the case of the thickness swelling and the internal bond strength, but more clearly, it is evident that the effect became flatter with an increasing PEI ratio. This might be due to the potential reaction between the free hydroxymethyl groups and the phenolic hydroxyl groups of the resol resin with the amino groups of the PEI prior to hot-pressing. These assumptions have to be proven in further investigations.

The results of the formaldehyde content determination are shown in Table 4.

Table 4. Formaldehyde Content in mg per 100g Panel at 6.5% Moisture Content

		UF	PF	
		10%	1.25%	2.5%
		3.163		
PEI	1.25%		0.267	
	2.5%			0.393

The perforator values show clearly that the HCHO content in the panels bonded with the PEI/PF mixture was lower by the factor 10 than in the UF bonded panels. This implies also lower HCHO emissions.

CONCLUSIONS

The investigations showed that it is possible to produce fibreboards with a mixture of PEI and PF that achieve comparable properties at an adhesive content of 3.75%. With a total amount of 5%, the properties largely exceed the 10% UF reference. These are promising findings in terms of the reduction of formaldehyde emissions.

A hypothesis was tested as to whether there are interactions between the two applied components or if it is sufficient to merely take the sum of the single effects into consideration. It was shown that there are interactions between PEI and PF and that the most appropriate ratio has to be determined. On the basis of the presented experiments it seems best to apply 1.25% PEI, as the effect is limited in combination with PF when exceeding the PEI ratio above this value. The most suitable PF ratio in these experiments was found to be 2.5%. To find the optimum proportion of PEI to PF for a specific application, further tests with more steps and a wider range have to be accomplished. To avoid a reaction between PEI and PF prior to hot-pressing, it might be expedient to combine PEI with a phenolic resin of the novolak type.

ACKNOWLEDGMENTS

The funding of this project by the Österreichische Forschungsförderungs-gesellschaft, within the FHplus project “Werkstoffe aus Holz” No. 811 450, is gratefully acknowledged.

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Article submitted: October 20, 2011; Peer review completed: November 27, 2011; Revised version received and accepted: January 3, 2012; Published: January 6, 2012.