

## Replacement of conventional dedusting agents with green alternatives in production of rock mineral wool insulation products

L. Mirnik,<sup>1,2</sup> S. Kovačič,<sup>1</sup> M. Huskić,<sup>1</sup> D. Pahovnik,<sup>1</sup> E. Žagar<sup>1</sup>

<sup>1</sup>Department for Polymer Chemistry and Technology, National Institute of Chemistry, Hajdrihova 19, Ljubljana 1000, Slovenia

<sup>2</sup>Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna Pot 113, Ljubljana 1000, Slovenia

Correspondence to: E. Žagar (E-mail: ema.zagar@ki.si)

**ABSTRACT:** The possibility to replace commonly used dedusting agents based on mineral oil with more sustainable vegetable oils as representatives of natural and environmental friendly materials is studied. Different anionic and nonionic emulsifying additives are studied as well. The stability of binder mixtures consisting of phenol-formaldehyde resin, urea, silane, and various dedusting agents is evaluated, and the adhesion of binder mixtures to the rock sand is analyzed by the sandbar test. Adequate stability of binder mixtures and high bending strength to break the bars are achieved when binder mixtures contained dedusting emulsions based on mineral or vegetable oil as well as their combination emulsified with lignosulfonate salt. The combination of mineral or vegetable oil with nonionic emulsifier on the other hand shows poor stability of binder mixtures. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44165.

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### INTRODUCTION

Fibrous insulating materials are used in building and industrial applications as thermal and sound insulation materials, molding compounds, wood composite materials, and so on.<sup>1–3</sup> In the production of thermal insulation material, a special binder mixture is used for gluing the fibers together to achieve desirable mechanical properties. For rock mineral wool production, the binder mixture typically consists of phenol-formaldehyde (PF) resin of resol type<sup>3–8</sup> and various additives, having their own specific function.<sup>9–15</sup> Typical additives in binder mixture are an amine, an activated silane, and a dedusting agent. The amine component (ammonium hydroxide or urea) stabilizes the medium pH and reacts with free formaldehyde present in water solution as a leftover of PF polymerization. The most commonly used silane component is alkoxy aminosilane, acting as a coupling agent between the PF and the mineral fibers,<sup>16</sup> whereby the silane's alkoxy and amine groups react with hydroxyl group on the fiber surface and with PF, respectively.<sup>15–17</sup> The dedusting agent in binder mixture reduces dust generation during installation of fiber insulation products or if they are otherwise handled.<sup>13–15,17,18</sup> According to Perander and Le Bell,<sup>9</sup> the task of the dust binding agent is to bind together any dust or to bind it to the main matrix body physically either through film formation or surface active properties. An additional benefit of using the dedusting agent in binder mixture is to provide the products with a certain level of hydrophobic properties.<sup>9</sup>

Commercially available dedusting agents are usually based on mineral oils of petroleum origin, typically prepared as the 55% water emulsions.<sup>13,18</sup> They differ with respect to exact chemical composition of mineral oil that depends on the source of crude oil. Mineral oils can contain different amount of aromatic fraction, which is considered to be unfriendly to the environment.<sup>9</sup> Since mineral oils are derived from the non-renewable sources, the plant oils obtained from the natural renewable sources have attracted increasing interest as the mineral oil substitute since they are of low cost, produced on a large scale, nontoxic, and readily available.<sup>19–21</sup> Dedusting agents differ also with respect to the emulsifier type.<sup>22</sup> In general, a lot of studies have been recently focused on the use of “green surfactants,” which are environmentally friendly, readily biodegradable and mostly derived from natural renewable resources.<sup>23,24</sup> The lignosulfonate salt originating from a natural material lignin can be considered as the sustainable anionic emulsifier in preparation of dedusting agents.<sup>23</sup> Lignosulfonates are generally produced as a by-product in manufacturing the paper from wood pulp. They are water-soluble polymeric compounds, and generally, they do not exhibit an amphiphilic structure, typical for conventional surfactants. Sinnige<sup>18</sup> studied the stability of binder mixtures containing dedusting agents based on the pure vegetable oils of different origin as well as the mixtures of mineral and vegetable oils. The results of this study revealed prolonged stability of binder mixtures when dedusting emulsions were stabilized with the lignosulfonate salt or poly(vinyl alcohol). Moreover, Budin

**Table I.** Chemical Composition of Dedusting Emulsions

Sample number	Composition	
	Hydrophobic component	Emulsifier
Sample 1	Mineral oil	Lignosulfonate salt
Sample 2	Mineral oil	Alkylated polyols and alkyl carboxylates
Sample 3	Mineral oil	Ethoxylated fatty acids
Sample 4	Mineral oil:vegetable oil = 3:1	Lignosulfonate salt
Sample 5	Vegetable oil	Lignosulfonate salt
Sample 6	Vegetable oil	Alkylated polyols and alkyl carboxylates
Sample 7	Vegetable oil	Ethoxylated fatty acids

*et al.*<sup>10</sup> found that up to 30% of PF in the binder mixture can be replaced by the lignosulfonate salt, since it is structurally similar to the phenolic resin. Namely, lignin as a polyphenol is capable of condensation reaction with formaldehyde or methylol groups of resol PF.<sup>2,10,25–27</sup> In addition, Hansen and Nissen<sup>14</sup> reported on improved stability of aqueous phenolic binder during transportation and storage if binder formulations are stabilized with various natural polymers (such as casein, soya protein, guar gum, arabic gum, ammonium alginate, and carboxylated cellulose).

Since mineral oils are derived from nonrenewable sources, the aim of the present study is to replace them with more ecologically sustainable dedusting agents based on “green” vegetable oils. For this purpose, different combinations of vegetable oil and emulsifier(s) were prepared in the form of emulsions and tested them as the potential substitutes for conventional dedusting agents. For this purpose, we prepared binder mixtures at a constant ratio of PF, urea, aminosilane, and particular dedusting emulsion and evaluated in the first place the time-stability of thus prepared binder formulations. In the next step, the sandbars were prepared from the rock sand and stable binding mixtures in order to study for the first time the binder mixture quality in dependence of dedusting formulation by evaluation of bonding strength of the binder mixture to the rock sand.

## EXPERIMENTAL

### Materials

A phenolic resin used was inorganic (KOH) catalyzed resol PF Prefere 72 5538M (Prefere Resins Company, Krems, Austria) delivered as 52% water solution with 15% urea added. 3-Aminopropyltriethoxysilane of 99.2% purity was supplied by BRB International BV (Ittervoort, Netherlands) with commercial name Silanil 919. Dedusting agents were the development samples with different chemical compositions of a hydrophobic component and an emulsifier and were supplied by the MDMG Invest-Chem d.o.o. (Šabac, Serbia). Dedusting agents were water emulsions with ~55 wt % solid concentration and up to 5 wt % of emulsifying agent added (samples 1–7). Their chemical composition is provided in Table I.

### Preparation of Dedusting Emulsions

Dedusting emulsions were prepared in 5-L Gauling’s double shield reactor. For 1 L of emulsion, 0.5 L of water was heated up to 80 °C. Then 50 mL of emulsifier(s) and finally 0.50 L of

hydrophobic component (mineral or vegetable oil or both) were added and mixed at 60 rpm for 1 hour. After adjusting (if needed) the solid content to 55%, the emulsions were transferred into laboratory homogenizer where they were homogenized at a pressure of 20 MPa. After that treatment, the emulsions were immediately cooled to 30 °C.

### Preparation of Binder Mixtures and Determination of Their Time Stability

First, the silane solution was prepared in a concentration of 2% (v/v) by the dilution of silane with water. Next, 1.2 mL of 2% silane solution and 1.3 mL of 55% solution of particular dedusting agent were mixed with 22 mL of resol PF resin. Thus, prepared mixtures were stirred and diluted with water to 80 mL. After slightly stirring the binder mixtures, they were left for up to a week upon which their stability was evaluated. If no phase separation or any other significant change occurred within a week, the binding mixtures were considered to be stable.

### Sandbar Preparation and Testing

The sandbars were prepared from the sand with similar chemical composition to that of rock mineral wool. Sand particles have typical diameter between 0.2 and 0.5 mm. The binder mixtures used to prepare the sandbars were prepared according to the procedure described above. Then, the particular binder mixture (80 mL) was mixed with the rock sand (800 g), and thoroughly stirred to ensure homogeneously coated sand with the binder mixture. Thus, prepared samples were set into metal moulds and cured at 180 °C for three hours. After cooling down the moulds in air for approximately an hour, the sandbars were taken out of the moulds. The weight of the sandbars was  $124 \pm 2$  g ( $\pm 1.6\%$ ). Later, two sandbars were tested for mechanical properties as “dry specimens,” whereas the other two were exposed to autoclave conditions (humidity: 100%, temperature: 120 °C, and elevated pressure: 2 bars) for 20 minutes. After taking the bars from autoclave, they were dried in an oven for 30 minutes at 105 °C, cooled down in air, and further tested for mechanical properties as “wet specimens.” With autoclave test the long-term stability of products is simulated.

The bending strength represents the force needed to break the bars. Bending strength, expressed in N/mm<sup>2</sup>, was determined by a Zwick-Roell dynamometer BZ1-MM14450.ZW01 and a testXpert® II software (Zwick, Germany). The results represent

an average value of two measurements. The lower acceptable limit of bending strength for “dry” and “wet” sandbars was internally set to 6 and 3 N/mm<sup>2</sup>, respectively. The values below these limits were considered to be too low and were indicative of poor binding mixture quality.

### X-ray Fluorescence Analyses

The sandbar experiments were performed with the rock sand, having the same chemical composition as the rock mineral wool. Sand composition was determined by a Spectro Xepos X-ray fluorescence (XRF) spectrometer and an X-LabPro software for data analysis. Prior to XRF analysis, ~10 g of sand was annealed for 3 hours at 550 °C. After cooling the sand to 20 °C, it was weighed (0.8000 g) and melted with a fusing agent (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>; 4.0000 g) at ~1200 °C to form the fused beds which were cooled to 20 °C. Then, the fused beds were inserted into XRF instrument to determine the content of constituting oxides (X<sub>n</sub>O<sub>m</sub>), that is, SiO<sub>2</sub>: 40.39%, CaO: 21.13%, Al<sub>2</sub>O<sub>3</sub>: 15.79%, MgO: 11.75, Fe<sub>2</sub>O<sub>3</sub>: 6.32%, Na<sub>2</sub>O: 2.16%, TiO<sub>2</sub>: 1.75%, and K<sub>2</sub>O: 0.27%.

### <sup>1</sup>H NMR Spectroscopy

The <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> on a Varian Unity Inova 300 MHz NMR spectrometer using a relaxation delay of 5 seconds, an acquisition time of 3 seconds, and tetramethylsilane (Me<sub>4</sub>Si, δ = 0) as an internal standard.

### Thermogravimetric Analysis

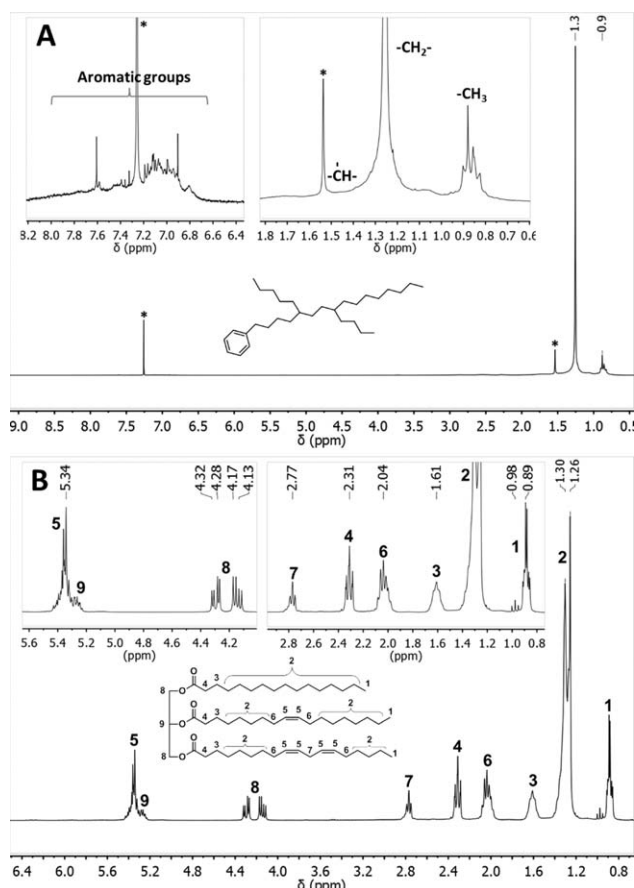
Neat lyophilized PF, the mixtures of PF and dedusting agent (sample 1) in a weight ratio of 90:10, both lyophilized before mixing, PF with added mineral oil (hydrophobic component of dedusting agent) in a weight ratio of 97:3 as well as PF with added lignosulfonate (emulsifier) in a weight ratio of 97:3 were analyzed with Mettler Toledo thermogravimetric analysis (TGA) instrument equipped with STARe 9.3 software (Mettler Toledo, OH, USA). The amount of typically 20 mg of sample was heated from 40 to 250 °C at a heating rate of 2 °C/min in the nitrogen flow of 20 mL/min.

## RESULTS AND DISCUSSION

The possibility to replace mineral oil with renewable and sustainable green alternatives, that is, vegetable oils, as a main component of dedusting agents used in production of rock mineral wool was studied. Since in the manufacture of fiber insulation products, it is advantageous to apply the binder and the antidusting agent simultaneously, the binder mixtures consisting of PF, urea, aminosilane, and particular dedusting emulsion had been prepared and after a week their stability in dependence of chemical composition of the dedusting emulsion was evaluated. Stable binder mixtures were further used for the preparation of sandbars for which the bending strength needed to break the bars was determined. From the results of sandbar test, we inferred on the adhesion strength and thus on the binder mixture quality for gluing the rock sand.

### Chemical Composition of Dedusting Emulsions

The chemical composition of mineral oil in dedusting emulsions denoted as samples from 1 to 3 was the same. It consisted of aliphatic hydrocarbons and a small amount of aromatic fraction [Figure 1(A)]. Samples 1–3 differed in the type of emulsifier, that is, sample 1 contained lignosulfonate salt, sample 2



**Figure 1.** <sup>1</sup>H NMR spectra of mineral oil (A) and vegetable oil (B), which were used for the preparation of samples 1–3 and samples 5–7, respectively. Sample 4 consisted of both oil types. \*Solvent CDCl<sub>3</sub> (7.26 ppm) and water in CDCl<sub>3</sub> (1.56 ppm).

contained a mixture of anionic (alkyl carboxylates) and nonionic (alkylated polyols) emulsifiers, and sample 3 contained ethoxylated fatty acids as a nonionic emulsifier (Table I).

Dedusting emulsions based on vegetable oil (samples 5–7) consisted of triglycerides, that is, the esters of glycerol and a mixture of saturated and unsaturated fatty acids [Figure 1(B)], and different types of emulsifier: sample 5 contained lignosulfonate salt, sample 6 contained a mixture of anionic (alkyl carboxylates) and nonionic emulsifiers (alkylated polyols), and sample 7 contained ethoxylated fatty acids as a nonionic emulsifier (Table I).

The hydrophobic part of the emulsion denoted as sample 4 consisted of a mixture of mineral and vegetable oils in a weight ratio of 3:1 and lignosulfonate salt as an emulsifying agent.

### Binder Mixture Stability

Since in the manufacture of fiber insulation products, it is advantageous to apply the binder and dedusting agent simultaneously to the fibers in order to increase production efficiency we determined the dispersibility of dedusting emulsions in a binder solution. For this purpose, we prepared the binder formulations consisting of PF with added urea, particular dedusting emulsion and silane in a volume ratio of 18.2:1.1:1.0 (see

**Table II.** Stability of Binder Mixtures after a Week and Results of Sandbar Tests

Sample number	Stability	Sandbar test <sup>a</sup>	
		$R_{\max}$ - dry (N/mm <sup>2</sup> )	$R_{\max}$ - AC (N/mm <sup>2</sup> )
Sample 1	Yes	10.4 ± 0.4	4.3 ± 0.2
Sample 2	Yes	8.6 ± 0.4	4.2 ± 0.1
Sample 3	No	—	—
Sample 4	Yes	9.7 ± 0.4	3.5 ± 0.1
Sample 5	Yes	6.8 ± 0.3	3.2 ± 0.1
Sample 6	Yes	3.6 ± 0.2	0.5 ± 0.1
Sample 7	No	—	—

<sup>a</sup> $R_{\max}$  is the bending strength representing the force needed to break the bars. DRY and AC denotations refer to "dry" and "wet" sandbars, the latter being exposed for 20 minutes to autoclave conditions (see Experimental section).

Experimental section). The final mixture was stirred and then allowed to settle. Typically, unstable binder mixture exhibits a clear separation of phenolic solution from emulsion with the oil phase rising to the surface. The results of stability of binder mixtures after a week of observation are summarized in Table II.

The binder mixtures prepared from PF, urea, silane, and the dedusting emulsions denoted as samples 1, 2, 4, 5, and 6 were homogeneous after a week of observation (Table II and Figure 2), and thus, they were considered to be stable. These binding mixtures were further used for the preparation of sandbars. The binding mixtures prepared from PF, urea, silane, and the emulsions denoted as samples 3 and 7 separated into two phases on the very next day, and therefore, they were not used for further testing experiments (Table II and Figure 2). Namely, phase separation of binding mixture in a holding tank or later at the nozzle end results in inhomogeneous fiber coating or clogging of the nozzles in fiber production. Both dedusting emulsions

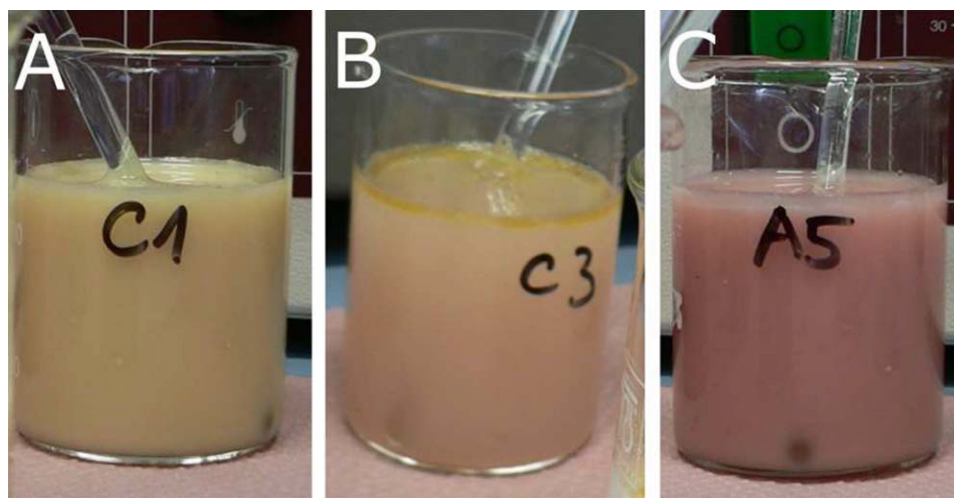
contained ethoxylated fatty acids as the nonionic emulsifier, which is, therefore, considered to be ineffective for stabilization of binding mixtures. These results are, thus, in agreement with those previously reported by Sinnige,<sup>18</sup> who found out that lignosulfonate salt as an emulsifier component of dedusting agent resulted in stable binding mixtures; however, the emulsifiers based on poly(ethylene glycol) caused the binding mixture to separate into respective phases.

Optical microscopy images of the binding mixtures prepared from the dedusting emulsions stabilized with lignosulfonate salt (samples 1 and 5) reveal the presence of oil droplets of ~2 μm in diameter [Figure 3(A,C)], whereas that of the binding mixture consisting of the dedusting emulsion stabilized with ethoxylated fatty acid does not show the presence of oil droplets dispersed in the continuous phase, but rather something like bicontinuous structure, indicating ongoing phase separation already on the very next day of binding mixture preparation [Figure 3(B)].

Since dedusting emulsions are extremely diluted within the binding mixtures we assume that stability of the interfacial phase (film) and not the droplet size is a key factor determining the overall emulsion stability. The presence of the resol PF resin in the continuous phase significantly affects the stability of interfacial film composed of ethoxylated fatty acids, resulting in phase separation of the binding mixtures composed of dedusting emulsions denoted as samples 3 and 7 through the sedimentation mechanism. On the other hand, the binding mixtures, consisting of dedusting agents stabilized with the lignosulfonate salt or a combination of alkylated polyols and alkyl carboxylates, appear to be stable even in the presence of the resol PF resin solution, which might be explained by the tougher interfacial film of the oil droplets surrounded by the charged surface, making these binding mixtures more stable.

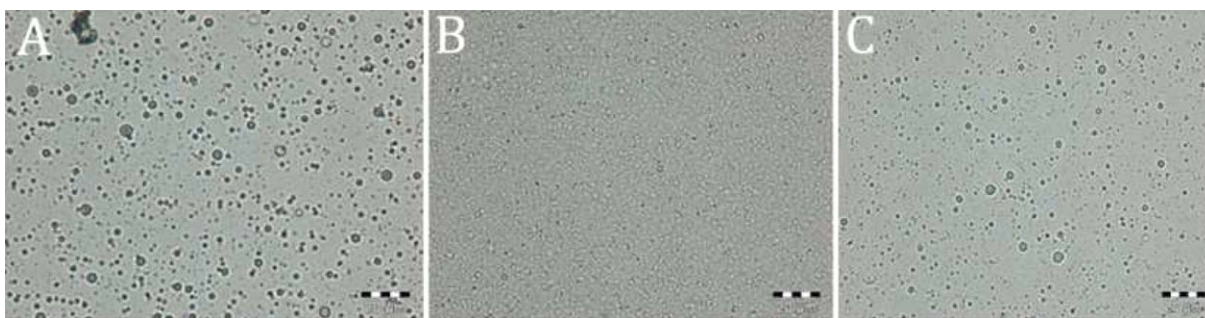
#### Sandbar Preparation and Testing

The quality of binder mixtures to glue the sand was tested in terms of bending strength by utilizing the sandbar test in order



**Figure 2.** Typical examples for stable (A and C) and unstable (B) binding mixtures. Binding mixtures consist of PF, urea, silane, and the following dedusting emulsion (A) sample 1, (B) sample 3, and (C) sample 5. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 3.** Optical microscopy images of the binding mixtures prepared from PF, urea, silane, and the following dedusting emulsions (A) sample 1, (B) sample 3, and (C) sample 5, after 1 day of observation; scale bar is 20  $\mu\text{m}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

to simulate the adhesion of binder mixture to mineral wool fibers on a large scale production. Therefore, the composition of selected sand for sandbars preparation was the same as that of rock mineral wool fibers (see Experimental section). The difference in mass of sandbars ( $\pm 1.6\%$ ) had negligible effect on the bending strength determination.

The highest bending strength for “dry” or “wet” state was obtained for the sandbars prepared from binding mixture in which the dedusting emulsion consisted of mineral oil and lignosulfonate salt as anionic emulsifier (sample 1, Table I). Sandbars prepared with binding mixture containing the dedusting agent based on mineral oil and a mixture of alkylated polyols and alkyl carboxylates as emulsifying system (sample 2, Table I) exhibited slightly lower bending strengths. For sandbars prepared with these two binding mixtures, the values for “dry” and “wet” states met the internally set criteria for acceptable bending strengths, that is, higher than 6 and 3  $\text{N}/\text{mm}^2$ , respectively. Results comparable to these were achieved also for the sandbars prepared from the binding mixture containing the dedusting emulsion based on a mixture of mineral and vegetable oils and the lignosulfonate salt (sample 4, Table I). Slightly lower results, but still within the limits, were obtained for a combination of pure vegetable oil and the lignosulfonate salt (sample 5, Table I). On the contrary, a combination of vegetable oil with emulsifying system of alkyl carboxylates and alkylated polyols (sample 6, Table I) gave much lower results, well below the target bending strengths.

#### Thermogravimetric Analysis

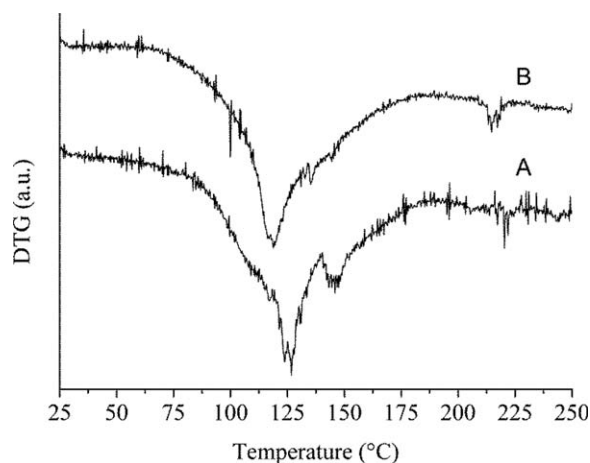
Since dedusting emulsions containing lignosulfonate salt as emulsifier showed the best results for bending strength irrespective of the oil type, its role was further investigated during curing the binding mixture using TGA at a low heating rate. The first derivative of the mass loss as a function of temperature (DTG) reveals the rate of reaction at a given temperature. Therefore, DTG curves of neat PF resin and PF resin with admixed dedusting agent (sample 1) were compared.

For the neat PF resin, the total mass loss of 35.0% was determined in the temperature range between 30 and 250  $^{\circ}\text{C}$ . This mass reduction is attributed mainly to the loss of the water due to condensation reaction and to a lesser extent to the emission of formaldehyde, remaining unbound in the resin. The loss of mass was implemented in three steps as can be observed from

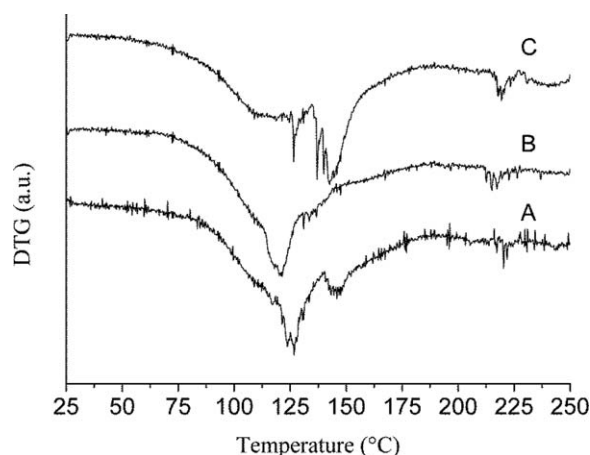
the derivative TGA curve (DTG) in Figure 4 (curve A). The first and the second steps overlapped in the range of 70–190  $^{\circ}\text{C}$  and revealed the peaks at 127 and 147  $^{\circ}\text{C}$ . The third and much less prominent step was observed in the range of 195–225  $^{\circ}\text{C}$  with the peak at 220  $^{\circ}\text{C}$ .

After the addition of dedusting agent (sample 1), the course of PF curing process changed, and the main peak was observed at lower temperature (119  $^{\circ}\text{C}$ ) (Figure 4, curve B). Changes in curing of PF resin were attributed to the influence of either emulsifier or hydrophobic component of dedusting agent. To get a better insight into the influence of individual components of dedusting agent on the PF curing process, the PF resin was mixed separately with the hydrophobic component (mineral oil) of emulsion as well as the emulsifier (lignosulfonate salt), and cured.

Lignosulfonate affected the rate of curing of phenolic resin by shifting the reaction towards lower temperature (Figure 5, curve B), whereas the addition of the mineral oil shifted the reaction towards higher temperatures (Figure 5, curve C). When these curves are compared to the DTG of a mixture of PF and dedusting agent (Figure 4, curve B), the conclusion can be made that emulsifier has the strongest influence on the curing kinetics of the PF by promoting the curing at lower temperatures. The involvement of lignosulfonate in curing performance



**Figure 4.** Derivative mass loss of neat PF resin (A) and PF resin with admixed dedusting agent (B).



**Figure 5.** Derivative mass loss of neat PF resin (A) and its mixtures with lignosulfonate salt (B) and mineral oil (C).

of PF resin was already studied.<sup>10,28,29</sup> In the study of Papadopoulou *et al.*,<sup>29</sup> it was also observed that curing temperature of the PF resin in the presence of wood (plywood panels) reduces as compared to the neat PF resin.

## CONCLUSIONS

The research was focused mainly on the possibility to replace mineral oil based dedusting agents with more sustainable natural materials of vegetable oils and “green” emulsifiers. Dedusting agents were mixed with phenol-formaldehyde resin, urea, and silane to determine the stability of the whole binder mixture. Finally, the sandbar test was performed as the preliminary test before the use of binder mixture in industrial production.

The conclusion after all testing showed that mineral oil based emulsions can be replaced with more sustainable natural vegetable oils especially when lignosulfonate is used as an emulsifier, most probably due to its participation in phenol-formaldehyde polymerization, creating sufficient level of adhesion strength between the binder and the sand. In that combination, the dedusting agents are composed of natural materials and thus promote the sustainability of the ecosystem and at the same time show comparable performance to that of the conventional dedusting agents based on mineral oils.

## ACKNOWLEDGMENTS

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