Lignonsulfonate-phenolformaldehyde Adhesive: A Potential Binder for Wood Panel Industries

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Summary: Spent sulfite liquor (SSL) was obtained from a paper mill based on grassy pulp material (bagasse, kaiggrass and wheat straws). Lignosulfonate (LS) was isolated from SSL by polymerization reaction, initiated with concentrated hydrochloric acid. Different adhesives were prepared by gradual replacement of phenol by LS in phenol-formaldehyde (PF) resole resin. The strength of these resins was evaluated by glue block shear test in two wood species, in both dry and wet states. Maximum shear strength and wood failure was obtained by 20% addition of lignosulfonate to PF resin. No significant difference was observed in shear strength and wood failure of the two wood species in dry and wet states indicating that the resin obtained is waterproof. The results obtained from this study were compared with different commercial glues. Our results were found better than these glues event at a ratio 50: 50 of PF to lignosulfonate.

Introduction

In the manufacture of particleboard, fiberboard and plywood [1] phenolformaldehyde and urea formaldehyde (UF) are most commonly used [2]. However during last few decades the increasing demand of particleboard / plywood and the rapid rise in the prices of petrochemicals from which the synthetic resins are derived has dramatically changed the economic picture of these industries. This has induced the scientist all over the world to carry out research on non-petrochemical phenolic compounds, such as lignin and tannins [2, 3].

Lignin is a natural polyphenol. The basic unit is composed of phenylpropane (C9) unites, which are linked together by C-C and C-O bonds. The supply of lignin is large, being the major by-product of pulping processes for papermaking; they constitute 24–33% of the woody substance in softwoods and 16–24% in hardwoods [4]. During sulfite pulping of wood the lignin is sulfonated [5] and is usually obtained as a by-product in the residual pulping liquor commonly referred to as "spent sulfite liquor"(SSL), consisting of mainly lignosulfonate, carbohydrate and inorganic salts [6]. The lignosulfonates are present as salts of cations such as magnesium, calcium, sodium and ammonium used as a base in the pulping operation [7-9]. Lignosulfonates has been found to be a more useful feed for the production of reactive lignins [5]. For adhesive purposes, these lignosulfonate need to be further polymerized to obtain useful adhesive properties. There are similarities between the structure of synthetic PF and lignin. Thus lignin can also react with formaldehyde and can be cross linked [10-15] with it. Keeping in view the similarity between the structure of the two compounds, many attempts have been made [16-20] on lignin obtained from pulping process of wood to co polymerize it with PF resin and to utilize it as a binder for plywood, hard board and particleboard.

Due to shortage of forest in Pakistan, our paper industry is totally dependent on grassy pulp materials, i.e. bagasse (Saccharum officinarum), kai grass (Saccharum spontarum) and wheat straws (Triticum vulgare). The waste product of these mills is either utilized as a fuel for the industry or discharged into river creating water pollution problem. Since no work has been done in this country to utilize and protect this precious organic material from wastage, this study was undertaken with an aim to copolymerize lignin obtained from spent sulfite liquor and gradually substitute it to PF resin. A series of resins so prepared were tested for their strength properties by glue block shear test in both dry and wet states. The results obtained from this study have been compared with commercial / standard glues.

Results and Discussion

Mean shear strength of glue joints from Shisham and Eucalyptus in dry and wet states by using glues, having different composition of PF and lignosulfonate are reported in Table-1. The higher
shear strength of the glue joints in Shisham is obvious from its higher density than Eucalyptus. In both wood species it is observed that shear strength increases with the increasing amount (up to 20%) of LS in the resin. Lignosulfonate being a huge polymer provided active sites on its benzene ring to copolymerize with PF during condensation reaction [5]. Further increase of LS in the resin decreases its shear strength. This may be for the reason that active sites are either occupied or hindered by the bulky groups inhibiting further condensation reactions. No significant difference is present in the dry and wet states indicating that the resins obtained are water resistant.

Table-1: Mean shear strength/wood failure of glue joints from shisham and eucalyptus in dry and wet states by using glues, having different composition of PF and lignosulfonate.

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>PF (%)</th>
<th>Load Kg</th>
<th>Shear Strength (Kg/cm²)</th>
<th>Wood Failure (%)</th>
<th>Load Kg</th>
<th>Shear strength kg/cm² Failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>100</td>
<td>0</td>
<td>2920</td>
<td>146</td>
<td>57</td>
<td>2347</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2155)</td>
<td>(100)</td>
<td>(71)</td>
<td>(2197)</td>
<td>(105)</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>3336</td>
<td>139</td>
<td>83</td>
<td>2715</td>
<td>142</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2233)</td>
<td>(113)</td>
<td>(83)</td>
<td>(2098)</td>
<td>(104)</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>3564</td>
<td>104</td>
<td>90</td>
<td>2956</td>
<td>155</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2401)</td>
<td>(137)</td>
<td>(84)</td>
<td>(2184)</td>
<td>(108)</td>
</tr>
<tr>
<td>70</td>
<td>30</td>
<td>2217</td>
<td>111</td>
<td>52</td>
<td>2088</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1883)</td>
<td>(96)</td>
<td>(49)</td>
<td>(1874)</td>
<td>(87)</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>1800</td>
<td>89</td>
<td>51</td>
<td>1768</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1869)</td>
<td>(88)</td>
<td>(44)</td>
<td>(1660)</td>
<td>(74)</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>1812</td>
<td>82</td>
<td>24</td>
<td>1753</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1368)</td>
<td>(71)</td>
<td>(23)</td>
<td>(1365)</td>
<td>(68)</td>
</tr>
</tbody>
</table>

Note: The values in the parenthesis represent the properties of Eucalyptus wood

Like shear strength the wood failure also increases with the addition of LS (up to 20%) in PF resin. No significant difference is present in the wood failure of the wood species in both states, which shows that the glue line is water proof. Similar results are reported by Nada et al. [18, 21]. They precipitated lignin obtained from different black liquors wasted from the cooking of rice straw, bagasse and cotton stalks, to produce pulp and paper. It is demonstrated that lignin can replace phenol by up to 40 per cent in phenol formaldehyde resin. The properties of the resin produced from bagasse lignin formaldehyde were found nearly the same as the resin International Standard (IS) produced from phenol formaldehyde. Terry Sellers [22] has modified phenol-formaldehyde resins with Kraft lignin. A variety of lignin types were found to be satisfactory bonding agents for hardboard, substituting for 25 to 100 percent of the PF control binder.

The results obtained from our study were compared with commercial glues (Dollar, Unilith, Mowilith 270, Crown and Calatac WD) applied to various wood species tested by Pakistan Forest Institute, Peshawar (Table-2). In Shisham wood maximum shear strength and wood failure was obtained with Dollar glue giving dry and wet strength values of 146 and 39kg/cm² and wood failure of 47 and 1.5 % respectively. In Eucalyptus, shear strength of 83 and 36 Kg/cm² and wood failure of 20 and 7.6% were obtained in dry and wet states, respectively. The results obtained from this study are well comparable to the commercial glues even at a 40% addition of lignosulfonate. Much better results were obtained in the wet state even at a 50% addition of lignosulfonate to PF resin. The synthesis and properties of these resins are reported elsewhere [23]. These resins were successfully utilized by the authors in the preparation of plywood and was tested both in the dry & wet states [cold water resistance (CWR), warm water resistance (WWR), boiling water resistance (BWR) and myological]. The glue shear load of the plywood in all the states met the requirements imposed by Pak. Std. 871, 1970. Wood failure of the plywood was compared with commercial standard (CS) 35-45 and the results found were equally good [24].

Table-2: Glue block shear strength/wood failure of different standard /commercial glue subjected to humidity changes.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Wood Species</th>
<th>Dry (65% RH)</th>
<th>Wet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shear strength (kg/cm²)</td>
<td>Wood failure (%)</td>
<td>Shear strength (kg/cm²)</td>
<td>Wood failure (%)</td>
</tr>
<tr>
<td>Unilith Shisham</td>
<td>122</td>
<td>43</td>
<td>55</td>
</tr>
<tr>
<td>(58)</td>
<td>(29)</td>
<td>(49)</td>
<td>(19)</td>
</tr>
<tr>
<td>Crown Shisham</td>
<td>52</td>
<td>12</td>
<td>25</td>
</tr>
<tr>
<td>(71)</td>
<td>(20)</td>
<td>(15)</td>
<td>(0)</td>
</tr>
<tr>
<td>Dollar Shisham</td>
<td>146</td>
<td>47</td>
<td>39</td>
</tr>
<tr>
<td>(83)</td>
<td>(20)</td>
<td>(36)</td>
<td>(8.0)</td>
</tr>
<tr>
<td>Mowilith 270 Shisham</td>
<td>109</td>
<td>13</td>
<td>34</td>
</tr>
<tr>
<td>(77)</td>
<td>(38)</td>
<td>(23)</td>
<td>(0)</td>
</tr>
<tr>
<td>Calatac WD Shisham</td>
<td>122</td>
<td>14</td>
<td>42</td>
</tr>
<tr>
<td>(82)</td>
<td>(50)</td>
<td>(24)</td>
<td>(0)</td>
</tr>
</tbody>
</table>

Note: The values in the parenthesis represent the properties of Eucalyptus wood

In this study, it has been observed that by increasing the amount of lignosulfonate in PF resin, the total solids increased and as the amount of glue required per shear area depends on the total solids of the glue, therefore greater are the total solids, lesser is the amount of glue required. This means that greater ratio of lignosulfonate in PF will require less amount of the glue for the same shear area to give more economical boards/plywood/glue joints.

Experimental

Black liquor was collected from Adamjee Paper and Board Mills Nowshera, NWFP, Pakistan, where sodium based sulfite pulping process is being
used. The mill is not utilizing SSL for any purpose and discharges it into the river Kabul as a waste product. Lignosulfonate was separated from the black liquor by polymerization reaction catalyzed by concentrated hydrochloric acid. Neat PF resins of resol type were prepared by condensation of phenol with formaldehyde using alkaline catalyst. A phenol molecule has three reactive sites. The first stage of reaction with formaldehyde gives five products of hydroxymethyl phenols in varying proportions depending on reaction condition. As the reaction proceeds further a network of phenol formaldehyde polymer is formed. Similarly different resins were prepared by gradually replacing phenol by lignin (up to 50% during copolymerization of lignin with PF adhesive by weight).

Table-3: Glue spread (152 g/152cm²) and total solids of different commercial glues compared with the PF-LS adhesives.

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Total solids (%)</th>
<th>Glue spread (g/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unileth</td>
<td>34.8</td>
<td>3.38</td>
</tr>
<tr>
<td>Crown</td>
<td>20.9</td>
<td>5.5</td>
</tr>
<tr>
<td>Dollar</td>
<td>23.3</td>
<td>4.9</td>
</tr>
<tr>
<td>Mowilith 270</td>
<td>34.0</td>
<td>3.36</td>
</tr>
<tr>
<td>Calatac WD</td>
<td>39.0</td>
<td>2.90</td>
</tr>
<tr>
<td>PF (100%)</td>
<td>25.6</td>
<td>4.46</td>
</tr>
<tr>
<td>PF:LS (90:10%)</td>
<td>52.3</td>
<td>2.18</td>
</tr>
<tr>
<td>PF:LS (80:20%)</td>
<td>58.0</td>
<td>1.97</td>
</tr>
<tr>
<td>PF:LS (70:30%)</td>
<td>59.3</td>
<td>1.92</td>
</tr>
<tr>
<td>PF:LS (60:40%)</td>
<td>60.2</td>
<td>1.89</td>
</tr>
<tr>
<td>PF:LS (50:50%)</td>
<td>62.9</td>
<td>1.81</td>
</tr>
</tbody>
</table>

**Glue Block Shear Test**

This test is intended to determine the comparative shear strength of adhesives, used for wood binding. Two types of wood species were used i.e. *Eucalyptus camaldulensis* and *Shisham delbergia sissoo*. The moisture content at the time of gluing was 9-10 %. The quantity of glue required for a pair of blocks (30.5 *5 *1.905 cm) was calculated on the basis of shear area and total solids of the resin. A single glue line was applied on the flat surface of the two blocks. A sufficient time (12 minutes) was allowed for initial setting of glue before the blocks were pressed at 150° C for 60 minutes. After conditioning period of one week, shear specimens were prepared and tested according to American Society of Testing Material (ASTM) [25]. The test for wet condition was carried out by keeping the specimens in a humidity chamber maintained at relative humidity (Rh) of 90% at 25 °C for seven days. The average shear strength of the glue joints at failure were measured under dry and wet states. The results obtained from this study were compared with the commercial glues tested by Pakistan Forest Institution, Peshawar.

**Conclusion**

It has been concluded from this study that SSL can be prevented from wastage by utilizing it in the synthesis of PF resole type of resin. 20% of phenol could be easily replaced by producing water resistant glue line with maximum glue strength and wood failure in both the states of the two wood species. Comparison with commercial glue indicates that PF-LS glue is water proof and has better strength properties even at a glue ratio 50:50 of PF to lignosulfonate. Also replacement of phenol by lignin in phenol formaldehyde resin has an economical effect and reduces the pollution caused by draining black liquor into rivers and streams.

**Acknowledgement**

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**References**