Synthesis of Phenolformaldehyde-Lignosulfonate Adhesive for Utilization as a Wood Binder

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Summary: Spent sulfite liquor (SSL) was obtained from Adamjee Paper and Board Mills, Nowshera, where different grasses (bagasse, Kaigrass and wheat straws) are being used as pulp material. Lignosulfonate (LS) was separated from SSL with the help of strong hydrochloric acid and characterized by UV and IR spectroscopy. A series of phenolformaldehyde-lignosulfonate (PF-LS) adhesive were prepared by gradual replacement of phenol (up to 70 % by weight) in the condensation reaction with formaldehyde by using alkaline medium. Various properties of the adhesive measured, indicate that phenol can be replaced by lignosulfonate up to 70 % without affecting the quality of the glue.

Introduction

One of the main sources of lignosulfonates or sulfonated lignins is the residual pulping liquors obtained in the pulp and paper industry where lignocellulosic materials such as wood, straw, corn stalks, bagasse and the like are digested with a sulfite or bisulfite to separate the cellulose or pulp from the lignin [1, 2]. The lignin is sulfonated [3] and is usually obtained as a by-product in the residual pulping liquor commonly referred to as "spent sulfite liquor". During sulfite pulping process of lignocellulosic material only half of the raw materials is obtained as a cellulosic pulp, while the other half forms spent sulfite liquor, consisting of mainly lignosulfonate, carbohydrate and inorganic salts [4]. The lignosulfonates are usually present in the liquor as a mixture of sulfonated lignins of various molecular weights varying from less than 1,000 to 100,000 and higher. The lignosulfonates and other sulfonated plant constituents are present as salts of cations such as magnesium, calcium, sodium and ammonium used as a base in the pulping operation [5-7]. The chemistry of lignin molecule is complex even in its unmodified form. The basic unit of lignin molecule is phenyl propane derivative. The macromolecule is supposed to be made up of these units, arranged in branched polyaromatic chains [8]. Lignin being a natural polyphenol has structural similarities with synthetic phenol formaldehyde and undergoes the same well-known reaction of phenol with formaldehyde through Methylene Bridge [9-14]. Keeping in view the structure of lignin, utilization of spent sulphite liquor from wood pulping has been developed and many attempts have been made [15-20] on lignin obtained from pulping process of wood to copolymerize it with PF resin and to utilize it as a binder for plywood, hard board and particleboard.

In a few paper mills, lignin from the black liquor is primarily used as a fuel during combustion of the waste product for the recovery of pulping chemicals, while in our country most of these industries are not utilizing the black liquor and it is thrown away into waterways causing serious hazards to the aquatic life.

Since in this country only a nominal portion of the total land is covered by forest, our paper industry is based on grassy pulp materials *i.e.* bagasse *(Saccharum officinarum)*, Kai grass *(Saccharum spontaneum)* and wheat straws *(Triticum vulgare)*. The lignin from these grassy materials is composed of guaiacyl-syringyl units where syringyl has been found to be the dominant unit [8, 20].

Keeping in view, the difference between the black liquor from wood pulp and that obtained from the grassy pulp, the present investigation is aimed at exploring the possibility of using lignosulfonate obtained from the grassy pulp as a partial replacement of phenol in preparing resol type of adhesive for

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plywood industry in this country. For this purpose resins in different concentration of PF and LS are synthesized and various properties have been measured.

Results and Discussion

Different properties of the glues studied are given in Table-1. Increase in density and viscosity of the glue by gradual replacement of phenol with lignosulfonate is obvious from the corresponding increase of total solids (Fig. 1). This is in accordance with the finding of Nada *et al.*, [21, 22] where lignosulfonate obtained from SSL based on rice straws as pulping material was used to prepare PF-lignosulfonate adhesives. They found that viscosity of the resin increases with the increasing amount of lignosulfonate in the adduct stage. This increase in the viscosity may be due to enhanced crosslinking between phenol, lignosulfonate and formaldehyde. The reflux time had to be decreased with the increasing amount of lignosulfonate in the adhesive, because the lignin based phenolic resins achieve higher viscosities more quickly than the pure phenolformaldehyde resin. This is probably due to the initial charge of polymeric fraction in the lignin based phenolic adhesive [23].

Table-1: Properties of PF-LS adhesive at different concentration of PF and lignosulfonate.

Adhesive (%)		pH	Density (g/cm^3)	Viscosity at 30°C	Total solids	Pot life	Glue curing time
PF	LS			(cp)	(%)	(days)	(minutes)
100	0	10.7	1.880	880	25.65	21	10
90	10	9.78	1.192	917	52.27	32	10
80	20	9.88	1.200	1003	58.07	45	10
70	30	9.78	1.206	1080	59.26	63	10
60	40	9.57	1.210	1155	60.20	90	10
50	50	9.55	1.224	1210	62.90	128	10
30	70	9.50	1.232	1322	65.00	147	10

Pot life of the adhesive also increased with the increasing amounts of the lignosulfonate in the resin (Fig. 1). This rise in pot life is most probably due to highly cross linked complex structure of PF-lignosulfonate adhesive. The active sites if any are hindered by the bulky groups and no further condensations are possible or activation energy required for further condensations is not achieved at room temperature. Therefore, rate of further condensation is very slow resulting in high pot life. However, pH of the glue and glue curing time at

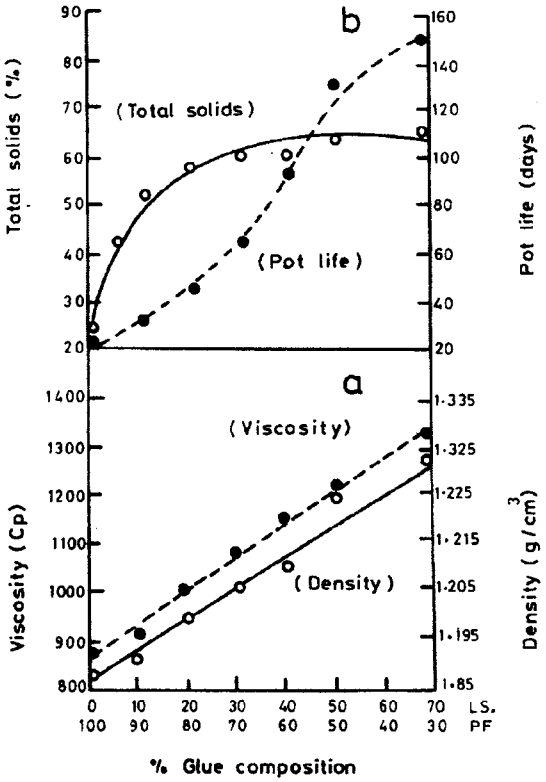

Fig. 1: Effect of lignosulfonate addition on a) viscosity and density b) total solid and pot life of a PF resin.

150 °C remained more or less constant for the adhesives prepared from different combinations of phenol formaldehyde and lignosulfonate. This is in accordance with the findings of Muller *et al.*, [23] which show that activation energies and cure rates determined by differential scanning calorimetry (DSC) showed no difference between adhesives and high lignin contents and had no inhibitory effects on adhesive cure. These resins were successfully utilized by the authors in the preparation of plywood and was tested both in the dry and wet states [cold water resistance (CWR), warm water resistance (WWR), boiling water resistance (BWR) and mycological]. The glue sheer 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].

Experimental

Black liquor sample was collected from the digester of the Adamjee Paper and Board Mills Nowshera, NWFP, Pakistan, where sodium based sulfite-pulping process is being used. Pulp material is mainly composed of biogases, kai grass and wheat straws. This paper mill is not utilizing SSL for any purpose and discharges it into the river Kabul. Lignosulfonate was separated from the black liquor through polymerization reaction catalyzed by concentrated hydrochloric acid. The isolated material was characterized by ultraviolet and infrared spectroscopy.

Synthesis of PF-LS Adhesive

Phenol, formaldehyde and sodium hydroxide were used at a fixed ratio of 100:110: 5 (by weight). The reaction mixture was refluxed for one and half hour at 105 ^{0}C and stirred vigorously with the help of a mechanical stirrer. At the end of reflux period, the flask was cooled under tap water to obtain a glue of suitable flow.

Similarly glues were prepared by gradual replacement of phenol with solid lignosulfonate, while the amount of formaldehyde and sodium hydroxide remained the same. Other reaction conditions were also the same except the reflux period, which had to be decreased with the increasing amount of lignosulfonate in the adhesive due to rapid rise in viscosity. Various properties of the adhesives were tested including pH of the glue, the density, viscosity, total solids and glue curing time at 150 ^{0}C. Pot life of the glue was also noted.

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