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The graft polymers from different species of lignin and acrylic acid: Synthesis and mechanism study

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ABSTRACT

The influence of lignin species on the grafting mechanism of lignosulfonate (from eucalyptus and pine, recorded as HLS and SLS, respectively) with acrylic acid (AA) was investigated. The graft polymers were confirmed by the absorption of carbonyl groups in the FTIR spectra. The decreasing phenolic group's content (Ph-OH) is not only due to its participation as grafting site but also to the negative effect of initiator. In the initial period (0–60 min), HLS and SLS both accelerate the polymerization of AA. Additionally, Ph-OH group's content is proportional to product yield ($Y\%$), monomer conversion ($C\%$) and grafting efficiency (GE%), strongly indicating that it acts as active center. Nevertheless, compared with HLS, $Y\%$ and $C\%$ in SLS grafting system are lower though it has higher Ph-OH group's content, which is due to the quinonoid structure formed by the self-conjugated of phenoxy radical in Guaiacyl unit. Finally, the lignosulfonate grafting mechanism was proposed.

1. Introduction

With the exception of cellulose, lignin belongs to the most abundant lingocellulosic resources. Large quantities of industrial lignin are produced from chemical pulping industry, annually generating about 60 million metric tons [1]. Nevertheless, most of lignin is burned as low cost of fuel, leading to the waste of resources and growing environmental problems. Therefore, great endeavors have been made on developing lignin-based materials since the early twentieth century.

Generally, grafting method is considered as one of the effective approaches for altering the properties of lignin. Functionalization of lignin with desirable monomers such as acrylamide, phosphorus–nitrogen intermediate, acrylic acid, dehydroabietic acid and methyl methacrylate can produce lignin-based biomaterials that have wide applications ranging from drilling mud thinner, flame retardant, aniline absorbent, binder, hydrophobic and high water resistance composite, compatilizer and so on [2–7]. Thus, in order to obtain high performance of lignin copolymers, it is necessary to conduct the studies on the lignin grafting mechanism. Nevertheless, because of its intrinsic properties, such as complex and inhomogeneous chemical structures, the researches on this aspect were hindered, mostly focusing on the role of phenolic group (Ph-OH) played in the grafting reactions [8–11].

Until now, there are still two opinions toward Ph-OH group's effect on the vinyl polymerization. First, it commonly acts as an inhibitor owing to its quinonoid structure. The formation of quinones group generated by the oxidation of Ph-OH group was observed in the graft copolymerization of lignosulfonate with acrylic acid (AA) which was initiated by chemo-enzymatic starts [10]. In addition, the evidences in the systems of grafting styrene onto either hydrochloric softwood lignin [12] or softwood lignosulfonate (having methoxyl group content of 8.8%) [13] both demonstrated that the percentage of monomer conversion ($C\%$) in the grafting reaction was relatively lower than that of homopolymerization. On the other hand, it is traditionally considered as an active center due to the declining content of it observed after the grafting reactions [8,11,14]. Besides, the initial rate of acrylic monomers polymerization (such as AA, acrylonitrile and methyl methacrylate) was considerably accelerated by the addition of softwood lignosulfonate [8,15]. Nevertheless, some researches indicated that the arguments for the active center should be strengthened. Recently, it has been reported that

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Abbreviations: Ph-OH, phenolic group; AA, acrylic acid; $C\%$, monomer conversion; H_2O_2, hydrogen peroxide; GE%, grafting efficiency; $Y\%$, product yield; HLS, eucalyptus lignosulfonate calcium; SLS, pine lignosulfonate sodium; THLS1, treated HLS by H_2O_2; TSLS1, treated SLS by H_2O_2; $K_2S_2O_8$, potassium persulfate; FTIR, Fourier transform infrared; DUV, Difference Ultraviolet spectroscopy; THLS, treated HLS by $K_2S_2O_8$; TSLS, treated SLS by $K_2S_2O_8$; HLS-AA, HLS graft polymer; SLS-AA, SLS graft polymer.

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Ph-OH group's content in kraft baggage lignin, and lignosulfonic acid would decline even only after treated by low hydrogen peroxide (H_2O_2) content (H_2O_2/lignin$_{wt}$ = 1–8%) [16,17], indicating that the decreasing content of it was not only associated with its role as grafting site as previous researches reported. In addition, the relationship between different Ph-OH groups' content and the corresponding of initial *C*% or the percentage of grafting efficiency (GE%) has not been established, which was more reliable evidence for judging the role of Ph-OH group. Therefore, further studies on its role should be conducted for elucidating the lignin grafting mechanism.

When it comes to the lignin species, extensive researches have been conducted on the lignin from softwoods which are mainly obtained from pine and spruce by different extraction methods, such as hydrochloride acid, sulfite, kraft and methanol–water methods [8,12,18,19]. In comparison to the softwood lignin, literature on the grafting of hardwood lignin is very little until now. With respect to the grafting styrene onto lignin compounds, Phillips reported that both softwood lignin compound (Guaiacol) and hardwood lignin compound (2,6-dimethoxyphenol) inhibited the polymerization of styrene under γ-irradiation, but the latter one was more reactive than Guaiacol [20]. However, the percentages of product yield (*Y*%) in the reactions of grafting acrylamide onto hardwood lignin (such as, aspen, polar and oak) were all higher than those from softwood lignin (pine and spruce) by using H_2O_2-$CaCl_2$ as a redox initiator, which may be ascribed to the higher content of sinapyl alcohol in the hardwood lignins [21]. Aimed at understanding the differences in the grafting mechanism between hardwood and softwood lignin, more basic investigations should also be performed. Eventually, focusing on the Ph-OH group and the above aspects would help to select the appropriate types of lignin to obtain the desirable performance of lignin graft polymers with high *Y*% and GE%.

The eucalyptus, a typical hardwood, was selected based on its great potential to be a raw material in the pulp and paper industry in the worldwide [22]. As for the representative of softwood, pine was choosed in view of its wide utilization in the researches. In this paper, the eucalyptus lignosulfonate calcium (HLS) and pine lignosulfonate sodium (SLS) were firstly treated by H_2O_2 (HLS/H_2O_{2wt} = 2%) to obtain the lignosulfonates with different Ph-OH group's content which were recorded as THLS1 and TSLS1, respectively. Then, the effects of different Ph-OH groups' content and lignin species on the corresponding of initial *C*%, *Y*% and GE% were compared. Finally, the influence of reaction conditions on *Y*%, *C*% and GE% was studied.

2. Experimental

2.1. Materials

The eucalyptus lignosulfonate calcium (HLS, ~96%) and pine lignosulfonate sodium (SLS, ~94%, $\overline{M_n} = 7000$, CAS: 8061-51-6) were purchased from Aladdin and Sigma–Aldrich chemical company, respectively. Acrylic acid (AA), potassium persulfate ($K_2S_2O_8$), hydrogen peroxide (H_2O_2, 30%) and hydroquinone are analytical reagents and obtained from the Kelong Chemicals Co. Ltd. (China).

2.2. Graft copolymerization of AA with lignosulfonates

The grafting reactions were carried out under a nitrogen atmosphere in a 100 ml three-necked flask equipped with a reflux condenser and magnetic stirrer. 1.6 g lignosulfonate was dissolved in distilled water (18.7 ml) at room temperature with constant stirring. The solution was immediately placed into the water bath and purged with nitrogen gas at least for 30 min. Then 8 g AA and the predetermined amount of $K_2S_2O_8$ were added into the flask. The nitrogen was supplied throughout the grafting reactions. The details of experimental conditions for grafting reactions of HLS and AA were recorded in Table 1. The graft copolymerizations of SLS and AA also were performed under the same parameters as these in HLS grafting system, thus detailed reaction conditions of them were not explained again.

Table 1
Experimental conditions for graft copolymerizations.

Sample[a]	HLS (g)	$K_2S_2O_8$ (g)	*T* (°C)	Time (h)
1	1.6	0.3	70	5
2	2.4	0.3	70	5
3	3.2	0.3	70	5
4	4	0.3	70	5
5	4.8	0.3	70	5
6	1.6	0.06	70	5
7	1.6	0.12	70	5
8	1.6	0.18	70	5
9	1.6	0.24	70	5
10	1.6	0.24	50	5
11	1.6	0.24	60	5
12	1.6	0.24	80	5
13	1.6	0.24	90	5

[a] Fixed conditions: AA = 8 g, H_2O = 18.7 ml, respectively.

After finished the grafting reactions, 0.2 g hydroquinone was added into the reaction solution to quench the reaction. Then, the solution was dried under vacuum (*P* < 0.3 MPa) at 70 °C until the weight did not change. Finally, the graft polymer was obtained by extracting the dried crude products with ethanol to remove homopolymer. *Y*%, *C*% and GE% were determined according to the method suggested by Chen [8].

2.3. Fourier transform infrared (FTIR)

FTIR spectra of the samples were done on a Nicolet 560 FTIR spectrometer using KBr pellet technique [23]. Each spectrum was recorded with 32 scans in the frequency range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}.

2.4. Difference Ultraviolet spectroscopy (DUV)

The content of phenolic hydroxyl (Ph-OH) groups was measured by DUV spectroscopy with the baseline method as described by Wexler [24].

3. Results and discussion

3.1. Changes in the Ph-OH group of lignosulfonate during grafting reactions

Traditionally, the decreasing Ph-OH group's content after grafting reactions indicates that it acts as an active center in the lignin copolymerization [8,11,14]. However, recent researches demonstrated that its content also would decline only under the treatment of initiators [16,17]. Thus, the residual content of it after initiators' treatment and grafting reactions was compared to illustrate whether it did as grafting site.

As illustrated in Fig. 1a, the original content of it in crude HLS and SLS was 1.56% and 1.64%, respectively. However, only after treated HLS and SLS by $K_2S_2O_8$ initiator (recorded as THLS and TSLS, respectively), it decreased by 8.3% and 9.1%, respectively. After the grafting reactions, its residual content in HLS and SLS was only 0.28% and 0.36%, which dropped by 82.1% and 78.0%, respectively. Compared with the decreasing trend caused by the treatment of $K_2S_2O_8$ initiator, the declining tendency for Ph-OH