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Graft polymers of eucalyptus lignosulfonate calcium with acrylic acid: Synthesis and characterization

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ABSTRACT

The graft copolymerization of eucalyptus lignosulfonate calcium (HLS-Ca) from hardwood and acrylic acid (AA) was investigated by using Fenton agent as a coinitiator. The influences of reaction conditions on grafting parameters i.e. product yield (*Y*%), AA conversion (*C*%), grafting ratio (*G*%) and grafting efficiency (GE%) were carefully studied. The effects of the phenolic hydroxyl (Ph-OH) group on the polymerization of AA and grafting reaction were researched. Graft copolymers were identified by the new absorption at 1727 cm^{-1}, more homogenized morphology and higher decomposition temperature after grafted with AA, as illustrated in FTIR, SEM and TG spectra. The optimum synthesis conditions are as follows: $H_2O_2 = 25.2$ mol/L, $FeCl_2 = 63.0$ mol/L, $T = 50\,^{\circ}C$ and $t = 2$ h and the optimum percentages of *Y*, *C*, *G* and GE are 97.61%, 95.23%, 71.29% and 78.85%, respectively. The Ph-OH group of HLS-Ca cannot inhibit the polymerization of AA and is involved in the grafting reaction as an active center.

1. Introduction

Around the world, over 50 million tons of lignin has been produced in the pulp and paper industry a year (Wang et al., 2011). The majority of it is only used as fuel to fire the pulping boilers or directly dumped into landfill space as waste (Derek, 2008). With the depletion of fossil fuel and the enhancement of environmental awareness, the grafting of lignin with functional monomer is viewed as an effective method of developing lignin-based materials, such as drilling mud thinner (Meister, Patil, & Channell, 1985), thickening agent (Meister, Lathia, & Chang, 1991) and sand stabilizer (Dong, Wang, & Zhao, 2008).

Current researches on lignin-based soil and sand stabilizers are focused on the commercial technical raw lignins, such as softwood lignosulfonate and kraft rice straw (Shulga et al., 2007; Xiao, Bolton, & Pan, 2007). It is known that the functional groups of lignin, such as carboxyl, carbonyl, hydroxyl or sulfonic acid groups can absorb on the edge of soil particles and bridge between them through intermolecular hydrogen bond, electrostatic or Van Der Walls attractions to form physical crosslinking (Ben-Hur, Malik, Letey, & Mingelgrin, 1992; Liu, Shi, Jiang, Bae, & Huang, 2009). Nevertheless, their effectiveness is suppressed by the low molecular weight and relatively low content of the above functional groups which are influenced by the botanical origin and extraction process (Li, Zhou, Wang, Zhong, & Song, 2003). Aimed at overcoming the above defects, the grafting of lignin with specific vinyl monomers is considered as a promising approach, which is adopted to append new functional groups onto lignin for increasing their absorption capacities onto soil particles. However, there have been few researches about the application of grafted lignosulfonate either from softwood or hardwood used as sand fixations until now.

Lignin is the natural polymer with a complex structure formed from three phenylpropanoid units of *p*-hydroxyphenyl (H), Guaiacyl (G) and Syringyl (S) which are linked by ether and carbon–carbon bond in an irregular form (Mohamad Ibrahim, Ahmed-Haras, Sipaut, Aboul-Enein, & Mohamed, 2010). Generally, the softwood lignin, such as spruce and pine, is predominantly derived from G unit. While in hardwood, such as eucalyptus, various ratios of S/G have been observed (del Río et al., 2005). Lignin is a high reactive bio-polymer with specific functional groups including hydroxyl (Xue & Tai, 1993) (phenolic and alcohol hydroxyl), aromatic C-5 hydrogen and benzyl hydrogen (Phillips, Brown, & Stannett, 1971). Depending on the original resource and functional groups for lignin, its suitability to be used in polymer modification can vary noticeably (Tejado, Peña, Labidi, Echeverria, & Mondragon, 2007).

Abbreviations: AA, acrylic acid; HLS-Ca, lignosulfonate calcium; *Y*%, product yield; *C*%, AA conversion; *G*%, grafting ratio; GE%, grafting efficiency; Ph-OH, phenolic hydroxyl; H, *p*-hydroxyphenyl; S, Syringyl; $FeCl_2$, ferrous chloride; H_2O_2, hydrogen peroxide; PAA, homopolymer; LS-AA, graft polymer; FTIR, Fourier transform infrared; DUV, difference ultraviolet spectroscopy; SEM, scanning electron microscopy; TGA, thermogravimetric analysis.

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For the grafting of lignin with various vinyl monomers, a number of studies have been performed on the lignin from softwood (Chen, Kokta, & Valade, 1979, 1980; Mai, Majcherczyk, & Hüttermann, 2000; Mai, Schormann, Hüttermann, Kappl, & Hüttermann, 2002; Meister & Chen, 1991; Phillips et al., 1971), which are obtained from pine and spruce by different pulping processes such as hydrochloride acid, sulfite, kraft and methanol–water methods. The vinyl monomers commonly used in the grafting reactions consist of acrylic acid, styrene, and acrylic amide. The grafting reactions can be initiated by irradiation (Phillips, Brown, & Stannett, 1973; Phillips et al., 1971), chemical initiators (Chen et al., 1980; Meister & Chen, 1991; Mohamad Ibrahim et al., 2010) or chemo-enzymatic starters (Mai et al., 2000) in appropriate aqueous or organic solvents. Most of researches on softwood lignin grafting mechanism were focused on the effects of phenolic hydroxyl (Ph-OH) group on the polymerization. There are two opinions on its effects. First, being a macromolecule with quinonoid structure, Ph-OH group usually acts as an inhibitor in vinyl polymerization (Chen et al., 1979; Phillips et al., 1973). Second, it can be involved in the formation of an active center on lignin for the decreasing content of it observed after grafting reaction (Chen, Kokta, Daneault, & Valade, 1986; Meister & Luo, 1993; Xue & Tai, 1993).

In contrast to the softwood lignin, the research work about the grafting of hardwood lignin is very little until now. In this research field, Meister et al. (1991) studied the effect of lignin species on the percentage of product yield in the grafting of acrylamide onto poplar, aspen and oak by using H_2O_2–$CaCl_2$ as a redox initiator. Phillips reported that hardwood lignin model compound (Syringyl) shows a retardative effect on the polymerization of styrene under γ-radiation (Phillips et al., 1973). In order to better understand the grafting of hardwood lignin with vinyl monomers, more basic and practical researches should be performed. The eucalyptus, a fast-growing and typical hardwood, shows great potential to be used as raw materials in the pulp and paper industry in the worldwide (Evtuguin et al., 2001). Thereby, an increasing amount of eucalyptus lignosulfonate is recovered after pulping process. In this paper, we investigated the possibility of grafting acrylic acid (AA) onto eucalyptus HLS-Ca by using Fenton agent (H_2O_2 and $FeCl_2$) as initiators. The effects of the grafting conditions on the products yield, monomer conversion, grafting ratio and grafting efficiency were carefully evaluated. The graft polymer was characterized by FTIR, SEM and TG. Finally, the effects of Ph-OH group of HLS-Ca on the polymerization of AA and grafting reaction were studied. The long term of this study is to fully utilize eucalyptus lignosulfonate as the raw material to produce the chemical modified bio-polymer which can be used as sand fixations.

2. Experimental

2.1. Materials

The eucalyptus lignosulfonate calcium (HLS-Ca, ~96%) was purchased from Aladdin Chemical Company. Acrylic acid (AA), ferrous chloride ($FeCl_2$) and hydrogen peroxide (H_2O_2, 30%) are analytical reagents and obtained from the Kelong Chemicals Co. Ltd. (China).

2.2. Graft copolymerization of acrylic acid and HLS-Ca

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. 8 g HLS-Ca 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. The predetermined amount of $FeCl_2$ solution and 8 g AA were added into the flask. Subsequently, H_2O_2 at the required content was added to induce the grafting reactions and a continuous supply of nitrogen gas was maintained throughout the reaction period. The details of experimental conditions for grafting reactions are recorded in Table 1. Unless indicated otherwise, the graft copolymerizations were all conducted at the following conditions: HLS-Ca = 8 g, AA = 8 g, H_2O_2 (mol/L) = 25.2, $FeCl_2$ (mol/L) = 63.0 at 40 °C for 2 h.

Table 1
Experimental conditions for the graft polymer synthesis.[a]

Sample	H_2O_2 (mol/L)	$FeCl_2$ (mol/L)	T (°C)	Time (h)
1	1.3	3.2	40	2
2	6.3	15.7	40	2
3	12.6	31.5	40	2
4	18.9	47.3	40	2
5	25.2	63.0	40	2
6	25.2	126	40	2
7	25.2	84	40	2
8	25.2	50.4	40	2
9	25.2	42.0	40	2
10	25.2	63.0	30	2
11	25.2	63.0	50	2
12	25.2	63.0	60	2
13	25.2	63.0	70	2
14	25.2	63.0	40	1
15	25.2	63.0	40	3
16	25.2	63.0	40	4
17	25.2	63.0	40	5

[a] *Fixed conditions*: 8.0 g HLS-Ca and 8.0 g AA.

After finishing the grafting reactions, all products were dropped into an excess of isopropanol under stirring. The mixture was centrifuged at 4000 r/min for 10 min. The upper suspension and precipitation obtained by centrifugation were dried under vacuum ($P < 0.3$ MPa) at 80 °C, respectively, until the weight did not change.

The powder from upper suspension which consisted of homopolymer (PAA) and partial graft polymer (LS-AA) was extracted with dioxane/isobutyl alcohol ($W_t/W_t = 6/4$) to remove PAA, then the residual solid mass was LS-AA; the powder obtained from precipitation which are composed of PAA, HLS-AA and unreacted HLS-Ca was extracted with ethanol and dimethyl formamide to remove PAA and LS-AA, respectively, then the residual solid mass was unreacted HLS-Ca. Product yield (Y%), AA conversion (C%), grafting ratio (G%) and grafting efficiency (GE%) were determined by the following formulas (Chen et al., 1986):

$$Y\ (\%) = \frac{W_t}{W_M + W_L} \times 100 \tag{1}$$

$$C\ (\%) = \frac{W_t - W_L}{W_M} \times 100 \tag{2}$$

$$G\ (\%) = \frac{W_L - W_{UL}}{W_L} \times 100 \tag{3}$$

$$\mathrm{GE}\ (\%) = \frac{W_t - W_L - W_H}{W_t - W_L} \times 100 \tag{4}$$

where W_t is the total weight of solid mass recovered from grafting reactions; W_M stands for the weight of AA monomer used in the grating reactions; W_L is the weight of crude HLS-Ca used; W_H is the total weight of PAA extracted from upper suspension and precipitation; W_{UL} is the weight of unreacted HLS-Ca obtained from precipitation.

2.3. Fourier transform infrared (FTIR)

FTIR spectra of HLS-Ca and LS-AA were recorded on a Nicolet 560 FTIR spectrometer using KBr pellet technique. Each spectrum was recorded with 32 scans in the frequency range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} (Dence & Lin, 1992).

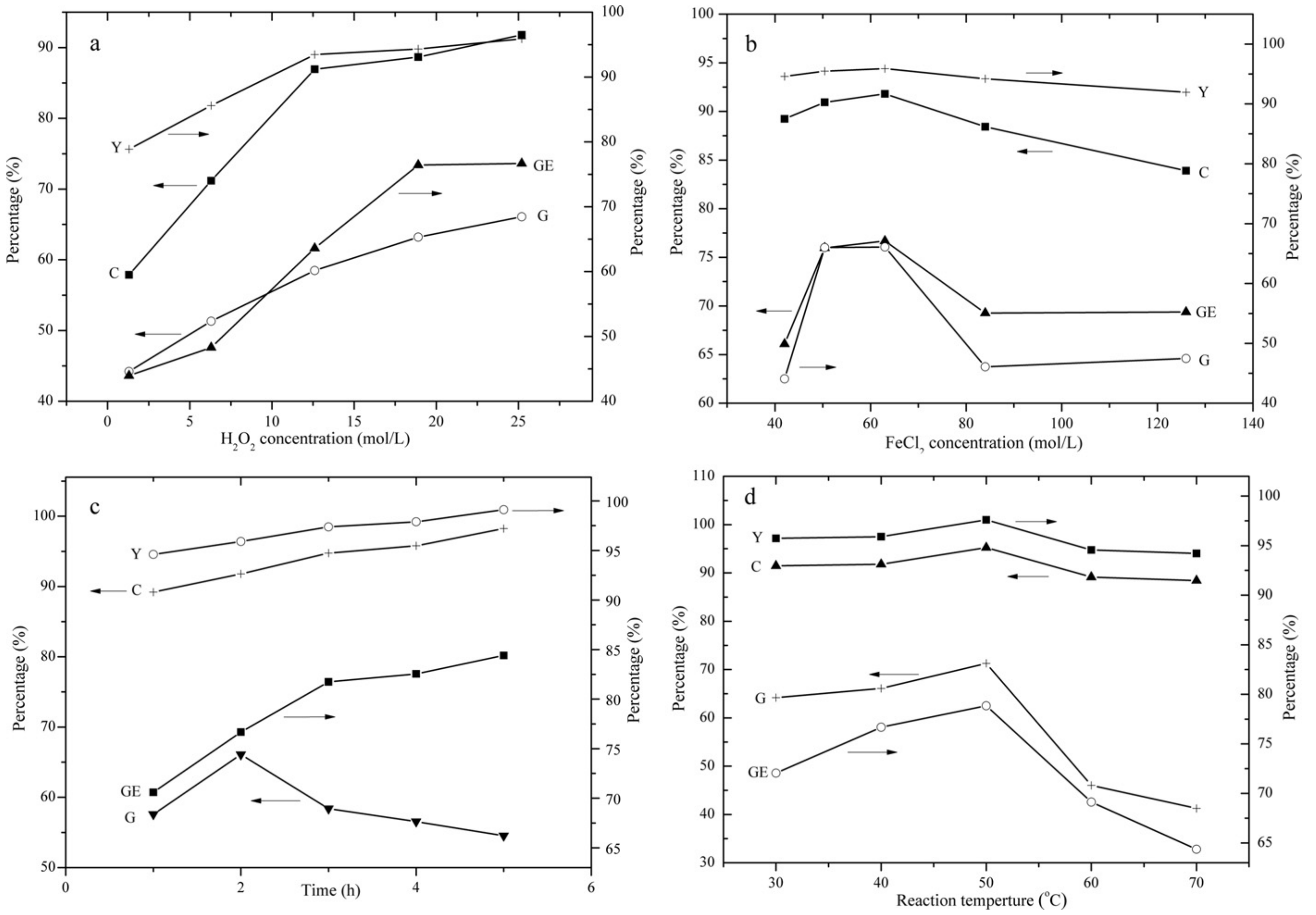

Fig. 1. The effect of reaction conditions on the percentages of *Y*, *C*, *G* and GE. The details of experimental conditions for grafting reactions are recorded in Table 1.

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 (1964).

2.5. Scanning electron microscopy (SEM)

The morphologies of HLS-Ca and HLS-AA were analyzed by scanning electron microscopy (JSM-5900LV).

2.6. Thermogravimetric analysis (TGA)

Thermogravimetric analyses were performed (DuPont SDT Q600) to determine the decomposition temperature of HLS-Ca and HLS-AA. The samples were heated from room temperature to 900 °C at the heating flow rate of 20 °C/min in nitrogen gas at the flow rate of 100 ml/min.

3. Results and discussion

3.1. The effects of reaction conditions on the graft copolymerization

3.1.1. The effect of H_2O_2 content

The content of H_2O_2 plays an important role in the control of the percentage of *C*, *Y*, *G* and GE. As illustrated in Fig. 1a, the percentages of *C*, *Y*, *G* and GE increase gradually with increase in H_2O_2 content up to 18.9 mol/L then beyond this value, they increase slightly. The maximum percentages of *C*, *Y*, *G* and GE reach 91.8%, 95.9%, 66.09% and 76.68%, respectively, when H_2O_2 content is up to 25.2 mol/L. The initial increase may be explained by the formation of a greater number of hydroxyl radicals and active grafting sites on HLS-Ca backbone with increase of H_2O_2 concentration (Chen et al., 1986). These radicals could in turn induce the production of AA homopolymers and graft polymers. The following trend in the percentages of *G* and GE after 18.9 mol/L may be attributed to the reduction in the number of grafting sites on HLS-Ca backbone. Similar results have been found for the graft copolymerization of softwood lignosulfonate from pine and AA monomers using Fenton agent by Chen et al. (1986).

3.1.2. The effect of $FeCl_2$ content

The effect of $FeCl_2$ concentration on the percentages of *C*, *Y*, *G* and GE is shown in Fig. 1b. The percentages of *C*, *Y*, *G* and GE increase up to 63.0 mol/L $FeCl_2$ concentration and then decrease with further increase in $FeCl_2$ content. The maximum percentages of *C*, *Y*, *G* and GE are 91.8%, 95.9%, 66.09% and 76.68%, respectively. This type of behavior can be expected, given that the property of redox pair initiator used in the grafting reactions. Along with the addition of $FeCl_2$, larger amount of hydroxyl radicals are produced by the reduction of hydrogen peroxide by ferrous ion. These radicals maybe in turn create lignin macro radicals, leading to the chain propagation of AA homopolymers and graft polymers. But at relatively higher concentration of ferrous ion, the excess ferric ion could inhibit free radical polymerizations, thus resulting in the decreasing percentages of *C*, *Y*, *G* and GE.

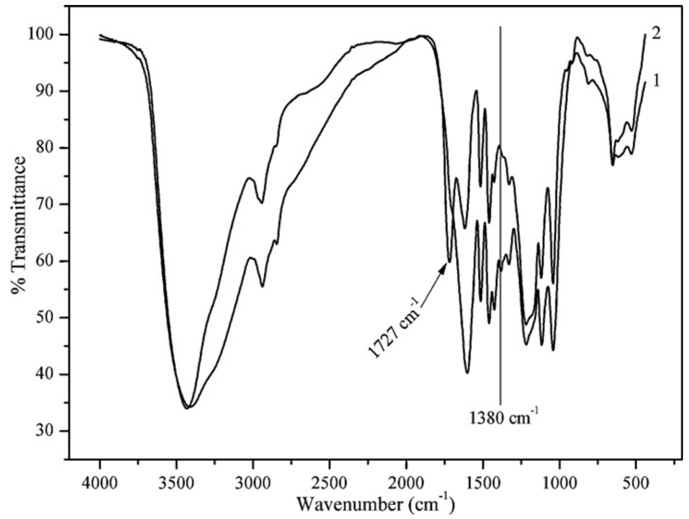

Fig. 2. FTIR spectra of graft polymer (spectrum 1) and HLS-Ca (spectrum 2).

3.1.3. *The effect of reaction time*

The effect of reaction time on the percentages of *C*, *Y*, *G* and GE was studied and the results are shown in Fig. 1c. The percentages of *C*, *Y*, *G* and GE increase gradually with the increase of reaction time up to 2 h, then after 2 h the percentage of *G* decreases but the other percentages still increase gradually. The percentages of *C*, *Y*, *G* and GE reach 91.8%, 95.9%, 66.09% and 76.68%, respectively, at 2 h. The increase in the percentages of *C*, *Y* and GE could be attributed to the addition of monomers to the growing grafted chains and the availability of hydroxyl radicals as well as monomers molecules. On the other hand, the former increase in the percentage of *G* may be due to the increase in the number of grafting sites on HLS-Ca backbone. Further with an increase in the reaction time, mutual annihilation of growing grafted chains, such as the termination reactions between HLS-Ca macro radicals, also occurs and leads to the decrease in the percentage of *G* (Chen et al., 1986).

3.1.4. *The effect of reaction temperature*

The effect of reaction temperature on the percentages of *C*, *Y*, *G* and GE is shown in Fig. 1d. The percentages of them increase when reaction temperature ranges from 30 °C to 50 °C, and then decrease with further increase in reaction temperature. The maximum percentages of *C*, *Y*, *G* and GE (95.23%, 97.61%, 71.29% and 78.85%, respectively) are observed at 50 °C. This trend can be ascribed to the increased diffusion rate of monomer and decomposition rate of H_2O_2 at higher temperature. Nevertheless, the decreased percentages of *C*, *Y*, *G* and GE by an increase in the temperature above 50 °C may be due to the favored chain termination reactions, chain transfer reactions and an increase in the formation of AA homopolymer.

3.2. *FTIR spectra of HLS-Ca and the graft polymer*

Fig. 2 illustrates the spectra of HLS-Ca before and after grafting reactions. The typical band of carbonyl group (unconjugated) at around 1727 cm^{-1} is absent in crude HLS-Ca, but this absorption can be observed obviously in HLS-AA, indicating the successful grafting of AA onto eucalyptus lignosulfonate. As can be seen from Fig. 2, the relative intensity of the band for non-etherified Ph-OH groups in HLS-AA, assigned at about 1380 cm^{-1} is much weaker than that observed in HLS-Ca (Dence & Lin, 1992). This result suggests that the attachment of poly acrylic acid chain onto lignosulfonate Ph-OH group could bring about the decreasing content of it after grafting reaction.

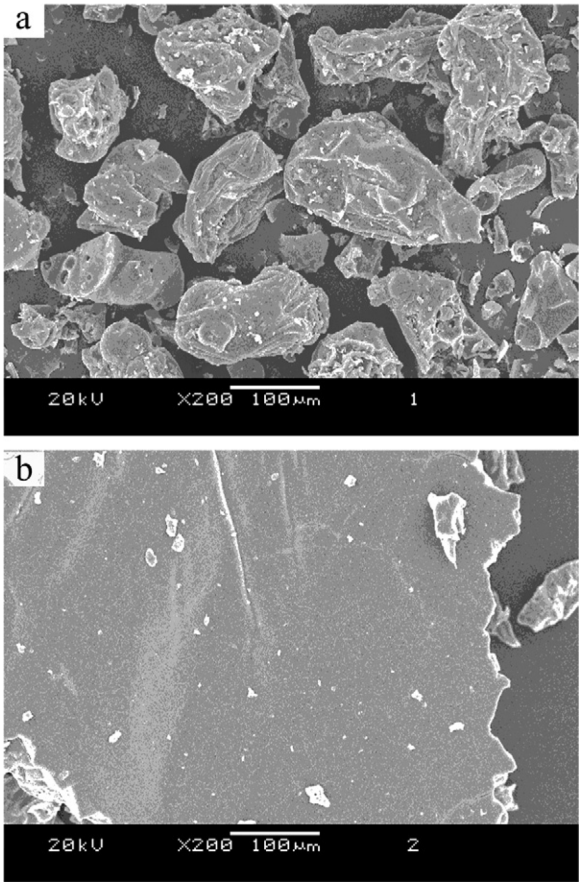

Fig. 3. SEM microphotographs of HLS-Ca (a) and LS-AA (b).

Typical hardwood lignin peaks could be observed in Fig. 2. The typical bands at 1328 cm^{-1} and 1116 cm^{-1} are associated with Syringyl structures in lignin molecules, while the signal at 823 cm^{-1} is assigned to G unit in lignin molecules. In addition, bands at 1037 cm^{-1} are identified with C—O stretching in S and G ring (Dence & Lin, 1992). These typical bands illustrate that eucalyptus HLS-Ca is a typical hardwood lignin. Moreover, band at 3412 cm^{-1} is assigned to aliphatic hydroxyl groups while the absorptions at 2939, 2839 and 1461 cm^{-1} are related to the C—H vibration of methylene and methyl groups (Mansouri & Salvadó, 2006). The stretching of C—C and C═C bands in the aromatic ring are recorded at 1513, 1604 and 1461 cm^{-1}, respectively.

3.3. *Surface morphology of HLS-Ca and HLS-AA*

The morphologies of HLS-Ca and HLS-AA is shown in Fig. 3. From the pictures, it can be observed that the morphology of HLS-Ca is greatly changed after AA grafted onto it. Before grafting reaction, HLS-Ca has a rough surface with shapeless configure and granular structure. In addition, some little pores disperse in its particles at random, which can facilitate the interaction of initiator, AA and solvent with HLS-Ca. After grafting reactions, the morphological image of LS-AA indicates much more harmonized structure with smooth surface. It could be contributed to the PAA chain grafted on the surface of HLS-Ca particles. Hence it can be concluded that AA monomer grafted on HLS-Ca successfully.

3.4. *Thermal decomposition of HLS and the graft polymer*

The thermal decomposition behavior of HLS-Ca and HLS-AA were studied by TG analysis. Compared with HLS-Ca (Fig. 4a),

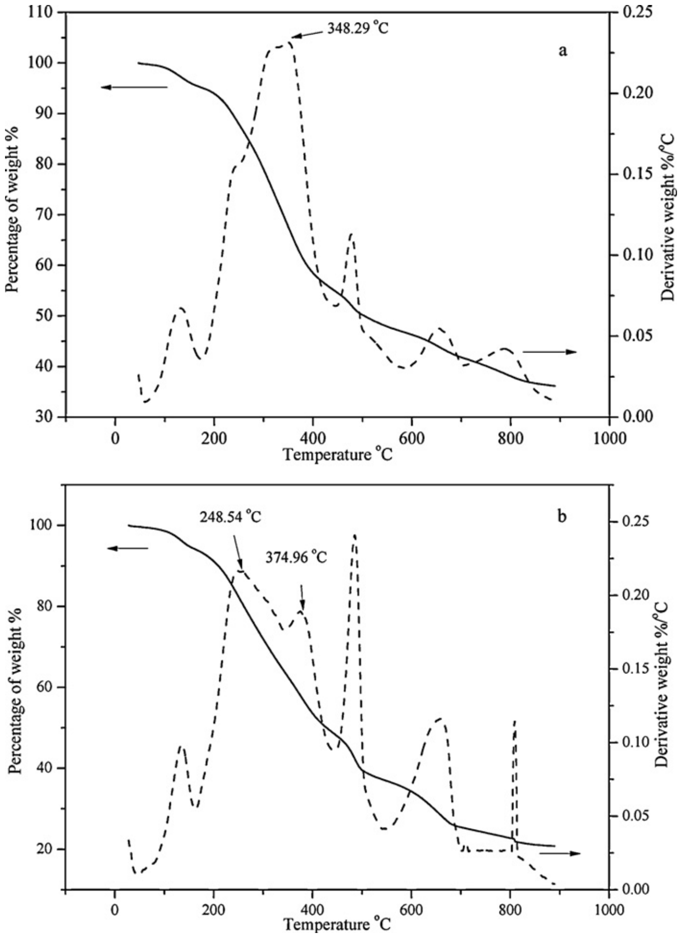

Fig. 4. Thermogravimetry analysis of HLS-Ca (a) and HLS-AA (b).

HLS-AA (Fig. 4b) exhibits a new decomposition peak at 248.54 °C, which is associated to anhydride decomposition from polyacrylic acid chain (Maurer, Eustace, & Ratcliffe, 1987). This new decomposition peak shows convincing evidence in the success of grafting AA onto hardwood lignosulfonate. Apart from that, another peak for the maximum decomposition of lignin backbone, assigned at 348.29 °C (Domínguez, Oliet, Alonso, Gilarranz, & Rodríguez, 2008) is greatly shifted to 374.96 °C, indicating that the thermal property of HLS-Ca could be improved by grafting with AA. The reasonable explanation is that the grafted polyacrylic acid chain is flexible and easy to coat tightly onto lignin surface. When HLS-AA exposes to heat, polyacrylic acid can melt and degrade at lower temperature, and it in turn prevents the heat to conduct directly to the lignin backbone (Lin, Zhang, Luo, Zhang, & Zhou, 2011).

The other decomposition steps of HLS-Ca and HLS-AA also are recorded in Fig. 4. The initial decomposition step in the range of 60.08–173.55 °C with 4.62% weight loss is mainly ascribed to the evaporation of water (both free water and bound water) and partly from the dehydration reaction (Lee & Fasina, 2009). The degradation of HLS-Ca within the range of temperature 173.55–252.39 °C (a shoulder peak in HLS-Ca DTG curve) with 7.62% weight loss is attributed to the break of lateral chain in HLS-Ca polymer (Shen, Gu, Luo, Wang, & Fang, 2010). At higher temperature (>440 °C), decomposition reaction, condensation reaction and secondary cracking of the phenolic compounds are possible during HLS-Ca and HLS-AA pyrolytic process (Domínguez et al., 2008).

Table 2
The residual content of Ph-OH group after grafting reactions.[b]

H_2O_2 (mol/L)	0	1.3	6.3	25.2
Ph-OH (wt%)	1.22	0.99	0.94	0.83

[b] *Fixed conditions*: AA = 8 g, HLS-Ca = 8 g, T = 40 °C, t = 2 h, $H_2O_2/FeCl_2$ (mol) = 4:1.

3.5. The effects of the phenolic hydroxyl (Ph-OH) group of HLS-Ca on the polymerization

3.5.1. The effect of Ph-OH group on the polymerization of AA

Most of researches about the grafting mechanism of softwood lignin with vinyl monomers were only performed on the Ph-OH group. It could act as active grafting sites in the grafting of lignin with vinyl monomers (Meister & Luo, 1993; Xue & Tai, 1993); on the other side, being a macromolecule like phenol structure, it might act as an inhibitor in the vinyl polymerizations (Chen et al., 1979; Mai et al., 2000; Phillips et al., 1971, 1973). Here, aimed at understanding Ph-OH group's effect from eucalyptus HLS-Ca on the polymerization of AA, the residual content of Ph-OH group after grafting reactions was determined by DUV spectroscopy and the results are shown in Table 2. It can be seen that the total unreacted content of Ph-OH groups decreases with the increase of initiator concentration, indicating that it may be oxidated to the quinoid structure or involved in the grafting reactions as an active center. In order to testify the hypotheses, AA conversion in grafting reactions was determined and compared with the value obtained for AA homopolymerization. Under the same reaction conditions, AA conversion (84%) during the grafting period of 5–30 min is obviously higher than that of value obtained in AA homopolymerization (33%). It may be concluded that the Ph-OH group in eucalyptus HLS-Ca has no inhibiting effect on the polymerization of AA but can considerably accelerate the initial conversion of AA. The similar results also were obtained in the grafting reactions of acrylonitrile and methyl methacrylate onto softwood lignosulfonate from pine (Chen et al., 1980). They ascribed these phenomena to the absence of quinonoid structure. In order to verify the above opinion, we treated HLS-Ca under the similar condition like grafting reaction except the addition of AA. The FTIR spectrum of treated HLS-Ca is shown in Fig. 5. It is found that the characteristic band of quinonoid structure at around 1645 cm^{-1} may be too weak to be observed in our experimental conditions, which is in agreement with the reason suggested by Chen et al. (1979). On the basis of little content of quinoid structure formed in the grafting reactions, finally it could

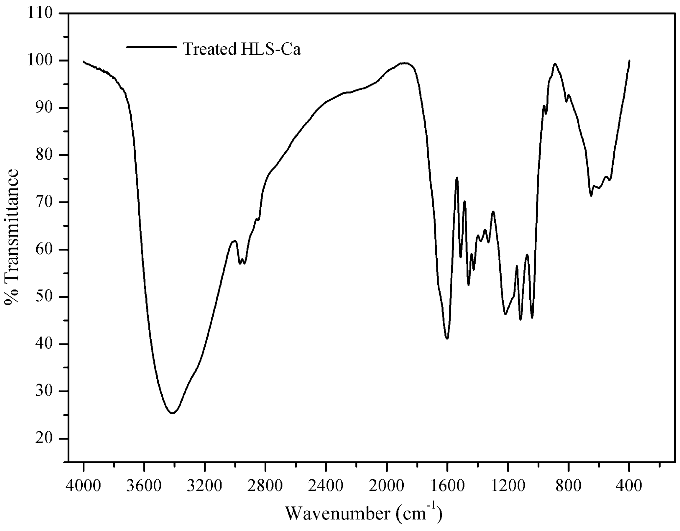

Fig. 5. FTIR spectrum of HLS-Ca treated by Fenton agent at 40 °C for 2 h, H_2O_2 (mol/L) = 25.2, $FeCl_2$ (mol/L) = 63.0.

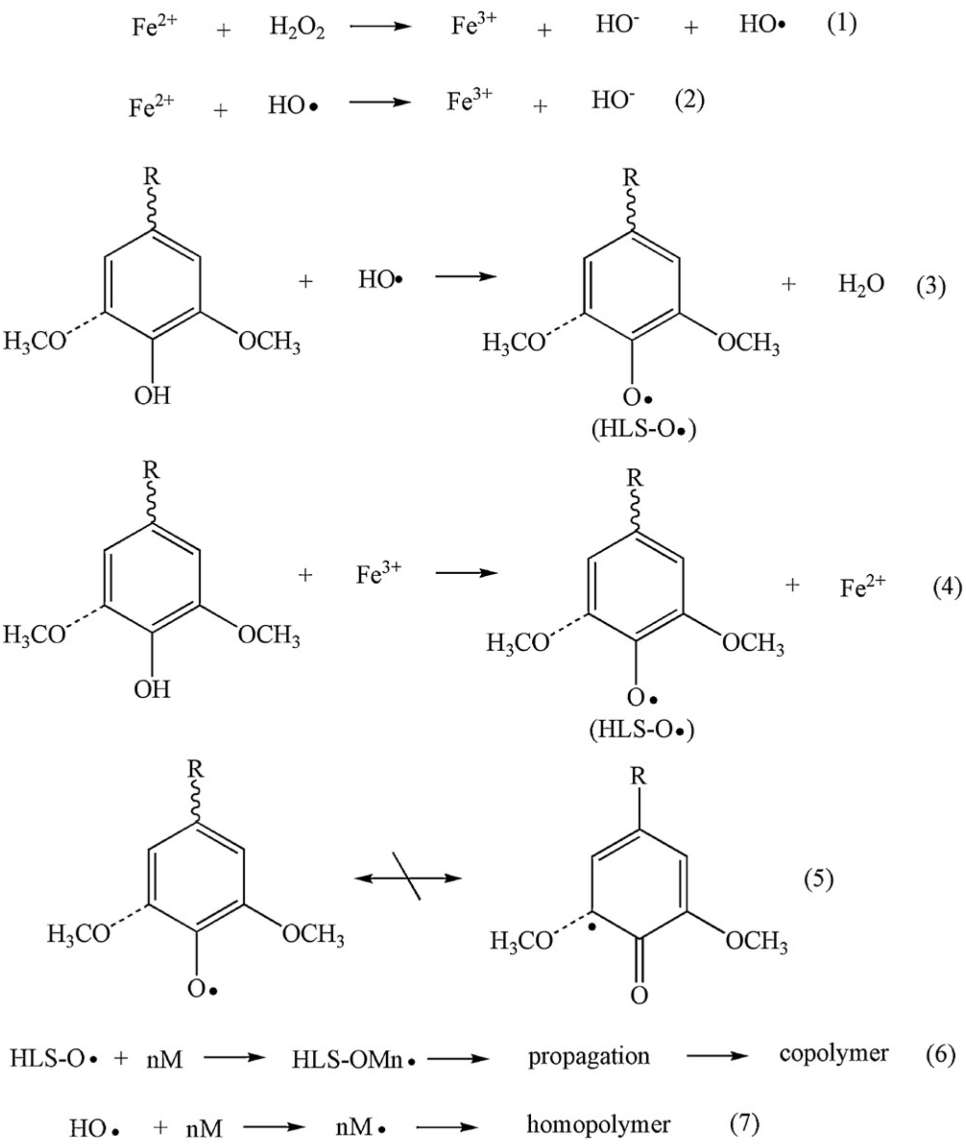

Fig. 6. Suggested reaction mechanism of grafting acrylic acid onto HLS-Ca.

conclude that Ph-OH group participated in graft copolymerization as grafting sites.

3.5.2. Mechanism of grafting copolymerization

In the initiating system containing H_2O_2 and Fe^{2+}, hydroxyl radicals formed by the reduction of H_2O_2 by Fe^{2+} (Reaction (1)) is able to start the homopolymerization of AA monomers (Reaction (7)) (Chen et al., 1986). In addition, hydroxyl radicals and Fe^{3+} could abstract hydrogen from Ph-OH group of hardwood lignosulfonate to produce phenoxy radicals (Reactions (3) and (4), respectively) which can accelerate the formation of graft copolymer and has been previously noted (Kislenko & Berlin, 1996; Kislenko & Oliinyk, 2003; Zheng, He, Qi, & Gao, 1995). It is assumed that once phenoxy radicals are produced, they can react with acrylic acid monomers so as to initiate grafting reactions (Reaction (6)). For the initial grafting process, the addition of hardwood lignosulfonate could accelerate the initial monomer conversion, which was supported by the results under our experimental conditions and also observed in the grafting of softwood reported by Chen et al. (1980). It is assumed that compared with the relatively short lifetime of hydroxyl radicals, the lifetime of phenoxy radicals could be longer. This may be attributed to the larger steric hindrance of lignin than that of hydroxyl radicals, which leads to the smaller possibility of quenching reactions between living radicals. Thus, compared with vinyl homo-polymerization, the higher content of living radicals (hydroxyl radicals and phenoxy radicals) may be responsible for the acceleration of initial monomer conversion in the grafting reactions. Another possible reason may be explained by the oxidation of Ph-OH group by Fe^{3+} (Reaction (4)), which would generate larger number of phenoxy radicals. With the propagation of acrylic acid chain onto Ph-OH group, the living grafted chains are obtained. Finally, these grafted chains are terminated by disproportionation, coupling or chain transfer between living radicals or radicals and macromolecules to form graft copolymer, so does the formation of homopolymer. The possible mechanism for grafting reactions is outlined in Eqs. (1)–(7), as shown in Fig. 6. The occurrence in the oxidation of Ph-OH group by hydroxyl radicals (Reaction (3)) is also suggested by the results that graft polymer (HLS-AA) can be obtained using only H_2O_2 as initiator. The possibility of proposed Reaction (4) was reported by Kislenko who found that the concentration of Fe^{2+} exceeds that of Fe^{3+} under neutral or alkaline solution in the absence of H_2O_2 (Kislenko & Oliinyk, 2003). The possibility of Reaction (5) is suggested by the little content of quinoid structure which was not observed by FTIR spectrum under our experimental conditions and is accordance with the results reported by Chen et al. (1979).

4. Conclusions

The acrylic acid monomer can successfully graft onto hardwood lignosulfonate calcium (HLS-Ca) from eucalyptus. Suitable conditions for graft copolymerization are as follows: $H_2O_2 = 25.2$ mol/L, $FeCl_2 = 63.0$ mol/L, $T = 50\,^{\circ}C$ and $t = 2$ h. Product yield, monomer conversion, grafting ratio and grafting efficiency could reach 97.61%, 95.23%, 71.29% and 78.85%, respectively. The morphological surface of HLS-Ca is homogenized and its maximum decomposition temperature can be increased from 348.29 °C to 374.96 °C after grafting with acrylic acid. The formation of quinonoid structure usually generated by the oxidation of phenolic hydroxyl group by H_2O_2 was hardly observed for the graft copolymerization of acrylic acid and HLS-Ca at our research conditions. The phenolic hydroxyl group is involved in the grafting reactions as an active center.

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