



Radiation-Induced Graft Polymerization of High Reactive Polyisobutylene on Lignosulfonate

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In this paper, the radiation-induced graft copolymerization between lignosulfonate and high reactive polyisobutylene (HRPIB) was studied. Radiation-induced graft copolymerization was carried out at room temperature without any additives and radiation doses are 30 mrad. It could change the physical and chemical properties of lignosulfonate and extend the application range of lignin. The reaction products should have potential applications in the field of adhesives, flocculants and rubber additives.

Key Words: Lignosulfonate, High reactive polyisobutylene, Graft polymerization.

INTRODUCTION

Lignin, cellulose and hemicellulose are the main components of plant skeleton. In the vegetables, the lignin only is inferior to cellulose in abundant and is important organic polymer. The lignin is widely distributed in the higher plants, which has vascular excluding of ferns and is the unique chemical components in gymnosperms and angiosperms. It is estimated that 150 billion tons of lignin can be produced in the world every year¹. In actual applications, the lignin is mainly obtained from industrial lignin. The vast majority industrial lignin is obtained from pulp and paper industry, in which lignosulfonate is widely used². Depending on the different processes of separation and extraction or different raw materials, the lignin generally divided into alkali lignin, lignosulfonate and other industrial lignin. Lignosulfonate is the main contaminants in pulping waste liquor, which are the main factors of pollution in rivers. The utilization of lignosulfonate can both abate a shortage of resources and ease the environmental pollution. It has enormous economic and social benefits.

The benzene propane is basic structural unit of lignosulfonate, which contains methoxy, hydroxyl (phenolic hydroxyl and alcohol hydroxyl), unsaturated double bond, sulfonate group and functional groups after the hydrolysis. Under certain conditions, they can be modified with a variety of substances and a variety of reactions, which include graft modification reactions. It generally includes three methods *viz.*, chemical grafting, biochemistry grafting and electrochemical grafting³.

The research on irradiation induced graft copolymerization between lignin and vinyl monomer have been studied by several scholars. Tetsuo *et al.*⁴ studied the graft polymerization between styrene and the hydrochloric acid lignin in γ -ray irradiation conditions. Phillips^{5,6} studied reaction conditions of irradiation graft between styrene and hydrochloric acid (or sulfuric acid) lignin. These studies work broadened to the application of lignin. However, the studies on the polymer-modified lignin have not appeared.

In this paper, the radiation induced graft polymerization between lignosulfonate and non-saturated low-level polymer (HRPIB) was studied. HRPIB usually refers to the oligomeric isobutylene. Oligomeric isobutylene is good in heat resistance, oxygen resistance, ozone resistance and expansion coefficient. The reaction energy is low and doesn't pollute the environment. It is a green chemical reaction. The polymer of lignosulfonate with HRPIB changes the physical and chemical properties of lignin, which provides a practical approach for the development and utilization of lignin.

EXPERIMENTAL

Lignosulfonate was purchased from Beijing Jiahe Technology Co., Ltd., high activity polyisobutene was purchased from Jilin Chemical Group Fine Chemicals Co., Ltd., ⁶⁰Co source was offered by Chang Chun Institute of Applied Chemistry of the Chinese Academy of Sciences.

In a typical experimental procedure, the powder of lignosulfonate was placed in a mortar. Then, HRPIB was added

and was grinded. Mixture was put into a plastic bag. The mixture was pressed into film out the air and the sample was radiated by ^{60}Co at 30 mrad for 24 h. It was washed with absolute ethanol and distilled water and then extracted by benzene in a Soxhlet extractor for 48 h, to remove the by-products. Finally, it was dried in vacuum at 60 °C for 5 h.

The structural analysis of the resulting products was determined by infrared on a Bruker-VECTOR22 Fourier transform infrared spectrometer. The grafting rate was measured by an ESCALAB Mark II X-ray photoemission spectrometer (XPS).

RESULTS AND DISCUSSION

The changes of liginosulfonate structure can be studied by infrared absorption spectra. Fig.1 shows the infrared absorption spectrum of liginosulfonate and grafted liginosulfonate.

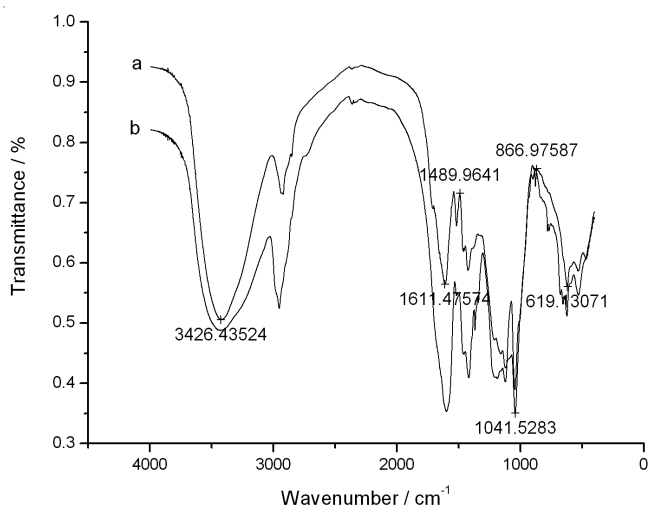


Fig.1. IR spectra of liginosulfonate before and after grafting reaction (a) the liginosulfonate; (b) grafted liginosulfonate

From the infrared absorption spectrum, it can be found the absorption peaks of methyl and methylene. The methylene (2920 cm^{-1} , stretching vibration, 1460 cm^{-1} , deformation vibration) is the characteristics of HRPB groups. The absorption peaks of methylene increased markedly in the IR of grafted liginosulfonate sample. The increase of the amount of saturated alkyl in the molecular structure of liginosulfonate indicates that the graft reaction has been occurred. The peak of $1800\text{--}1600\text{ cm}^{-1}$ region can be attributed to $>\text{C}=\text{O}$ or $\text{C}=\text{C}$ double bond in the infrared spectra. It can be seen that the peak of 1611 cm^{-1} obviously increased, which shows the changes of carbonyl content.

Liginosulfonate is aroma compounds, has the characteristic of absorption ultraviolet light. In the UV spectrum, the benzene ring has three conjugated double bonds, their transition characteristic absorption band on the $\pi\rightarrow\pi^*$ are: E_1 locates at 180–184 nm, $\epsilon=47000$; E_2 locates at 200–204 nm, $\epsilon=7000$; B locates at 230–270 nm, $\epsilon=200$. The benzene ring of liginin structure contains substituents, the band of B is simplified and has red shift. It has a stable absorption peak at the 280 nm. The UV absorption spectra of liginosulfonate is formed by additive absorption spectra of constituent units, it shows a monotonous,

dull and mellow. Thus, it can be seen that the peak of UV absorption spectrum of liginin is obvious near the 205 nm and 280 nm (Fig. 2).

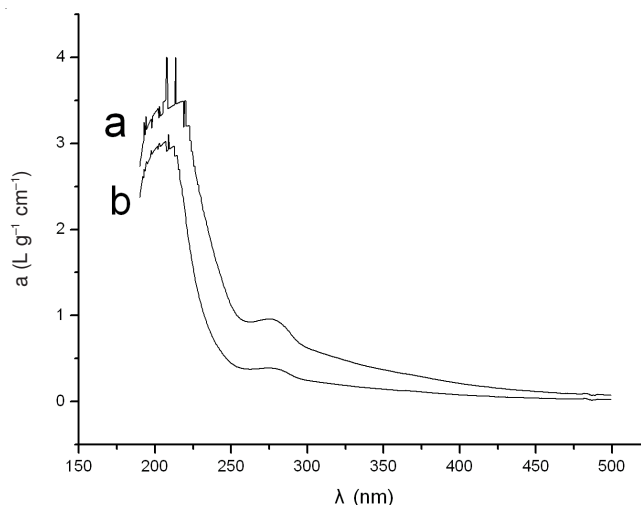


Fig.2. UV spectrum of liginosulfonate (a) and grafted liginosulfonate (b)

The HRPB, which is grafted on liginosulfonate has a large steric effect. Its double bond become saturated substituted alkanes. Steric hindrance excludes substituents from the benzene ring plane, which conjugates with the original benzene ring. The electron of substituent can not be overlapped fully to p system of benzene, which affects the spectrum. Grafted product absorption curve (Fig. 2b) maintains the original form of liginosulfonate spectrum, but the intensity of absorption peak reduces due to steric factor at 280 nm. It was hypochromic effect which is influenced by alkyl chain length and counts. The molecular chains of HRPB have the same length, the reduction of the absorption peak intensity is due to the amount of HRPB molecules grafted on the liginosulfonate. The changes of the hydroxyl phenol on liginosulfonate can be reflected by the changes of liginosulfonate absorption peak near 205 nm.

From the XPS spectra, it can be found that contents of the methoxyl on liginosulfonate will reduce after irradiation reaction. It can be speculated that de-methoxy-reaction is occurred in irradiation grafting process. The reaction makes absorption peak of grafted polymer near 205 nm blue-shift in the UV spectrum.

The content changes of different groups on the liginosulfonate are analyzed by the X-ray photoelectron spectroscopy. Fig. 3a shows the X-ray photoelectron spectroscopy (XPS) of liginosulfonate and Fig. 3b shows the XPS of graft polymer of liginosulfonate. C and O elements of XPS are discussed and other factors are ignored in this paper. Comparing two figures, the contents of C element of the grafted liginosulfonate is higher than liginosulfonate in the XPS pattern and the content of O elements is lower. It is can not be avoided that the oxygen is adsorbed on the surface of sample. Thus, the reduction of the O elements does not explain that the O element of molecular has changes in the sample. Reduction of O elements peak is referred to adsorption properties of the modified liginosulfonate, which can be described as an indirect explanation of the surface structure changes of modified liginosulfonate. HRPB is non-

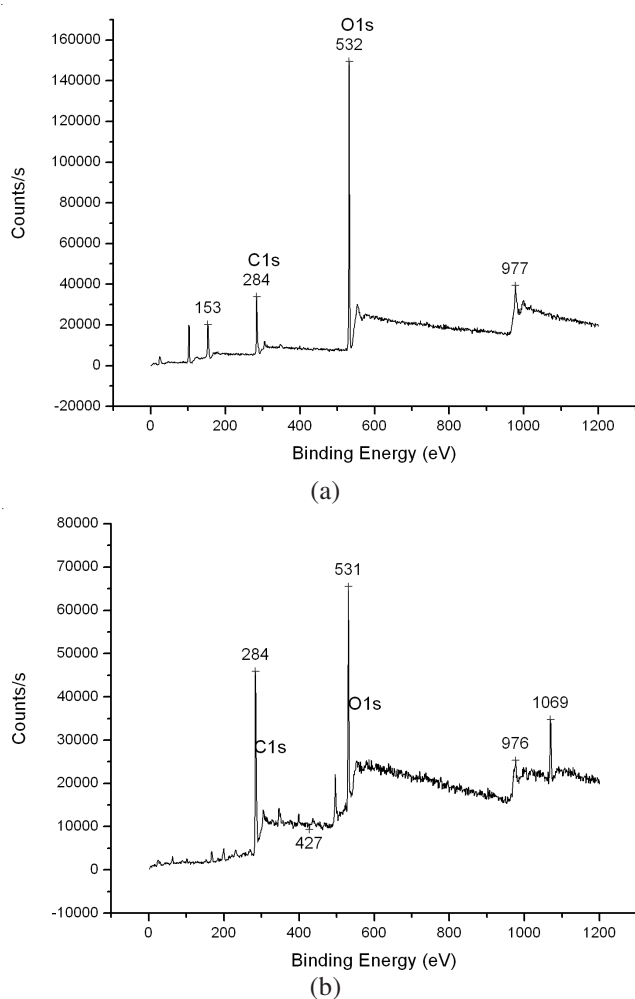


Fig. 3. XPS pattern of lignosulfonate (a) and grafted lignosulfonate (b)

polar organic compounds, which takes graft polymerization reaction on the surface of the lignosulfonate molecule, reduces the polarity of lignosulfonate surface and changes the adsorption properties of the surface of sample film. The adsorption ability of the surface of graft polymers membrane debase. The increase of the C element content shows the changes of surface structure, which shows a new group to connect on the surface of three-dimensional structure of lignosulfonate. The C1s peak of XPS can be fitted into four main characteristic peaks, which are the benzenoid C, carbonyl C, methoxy C and methylic C which links up with methenyl-methyl. Their binding energies are located at 284.28, 288.61, 286.9 and 285.56 eV (Fig.4.).

The content changes of characteristics groups are shown in Table-1. The methyl is the characteristics of HRPiB unit. Table-1 shows that the content of methyl has an increase of 42.86 % in the lignosulfonate structure after irradiation graft reaction. It proves that the graft reaction of lignosulfonate has been occurred and the HRPiB amount of grafted lignosulfonate molecules reflects reaction extent more accurately. It proves that de-methoxy reaction of the site of C5 in benzene ring is more conducive to graft reaction of lignosulfonate. The data shows that the methoxy content in modified lignosulfonate decreases 38.8 % in irradiation reaction. It fully shows that the methoxy-off reaction has been occurred at the C5 position

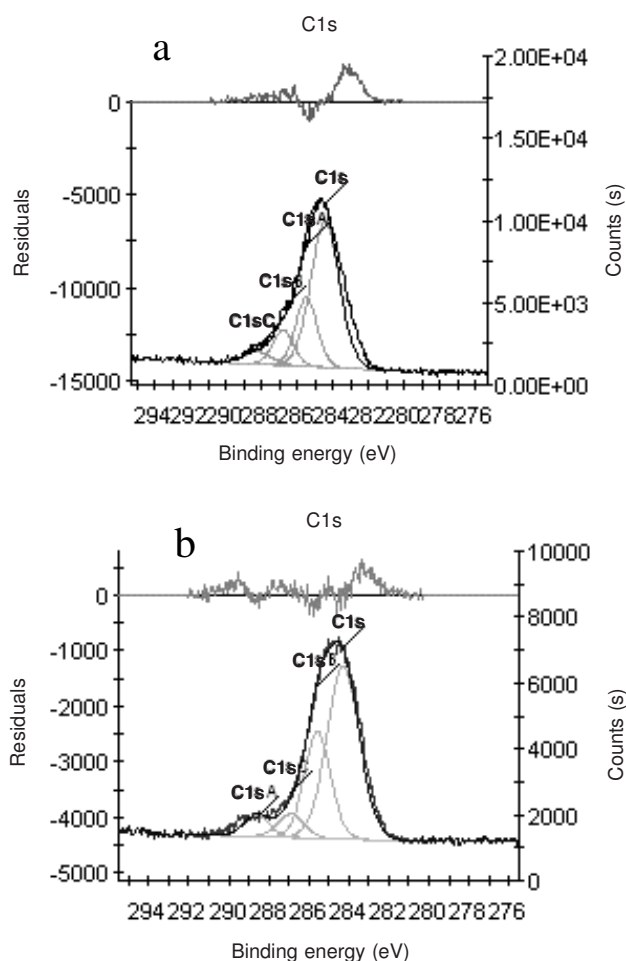


Fig. 4. C1s pattern of lignosulfonate (a) and grafted lignosulfonate (b)

of the benzene ring under the irradiation conditions and the graft copolymerization has been occurred at the connection of the C5 methoxy position. The reasons of carbonyl content change have been discussed in the infrared spectrum.

TABLE-1
CHANGES OF CHARACTERISTICS GROUPS OF GRAFTED LIGNOSULFONATE

Characteristic Group	Area Ratio of CPS		Changes of Content Relative
	Lignosulfonate	Grafted Lignosulfonate	
Benzenoid, 284.28eV	1.00	1.00	
Carbonyl, 288.61eV	0.08	0.10	+25 %
Methoxy, 286.90eV	0.18	0.11	-38.8 %
Methyl (HRPiB), 285.56eV	0.35	0.50	+42.86 %

The glass transition is a universal phenomenon in polymer and the glass transition temperature (T_g) of amorphous polymer is one of the most important physical parameters. In the graft polymerization reaction, the replace group's steric hindrance and flexible of branched-chain have a significant impact on T_g . Glass transition temperature will rise along with increasing of the chain internal rotation steric hindrance and substituent

size of molecule. But, T_g is not improved when the size of branched-chain increases. If the branched-chain of the base is flexible, the bigger branched-chain of the base will go with the greater the flexibility, it is equivalent plasticizer under the presence of flexible branched-chain and T_g declines. Fig. 5a shows that lignosulfonate in the pre-irradiation has two T_g transition points. The first is causative of small molecule impurities existing in the lignosulfonate. The second is the glass transition temperature of lignosulfonate. T_g is 192.85 °C. Fig. 5b shows the DSC of grafted lignosulfonate. It can be seen that there is only one temperature change in the curve. It shows that graft copolymer of lignosulfonate is after extracted by Soxhlet extractor. Glass transition temperature is 127.746 °C, the T_g is lower 65.104 °C than the pre-modification. It shows that the lignosulfonate glass transition temperature decreases when the HRPIB (a flexible long-chain alkane) grafts on the lignin. The lower glass transition temperature is conducive to the development and utilization of lignosulfonate.

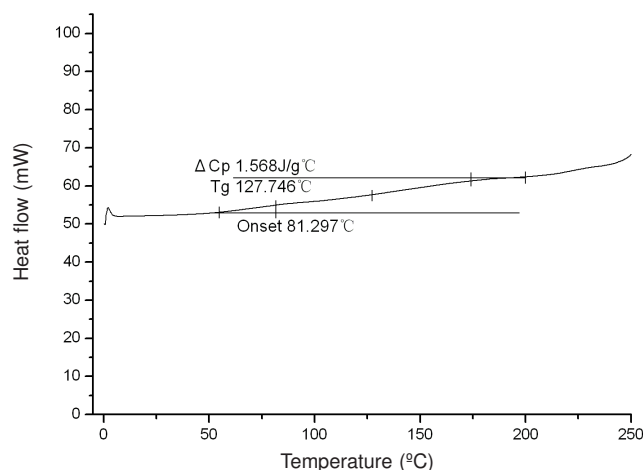
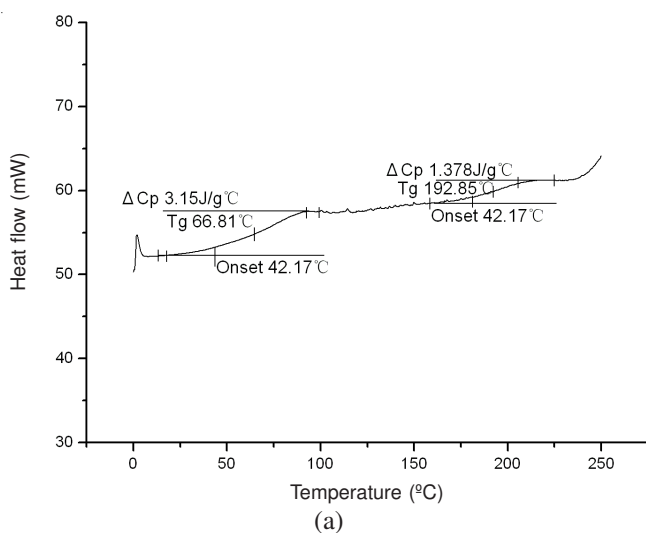


Fig. 5 DSC curves of lignosulfonate(a) and and grafted lignosulfonate (b)

Conclusion

By radiation-induced, HRPIB can be grafted copolymerization with lignosulfonate. The reaction is carried out at room temperature, radiation dose is 30 mrad and the irradiation time is 24 h. The reaction between di-methoxy and carbonyl can be occurred during irradiation graft reaction. It is beneficial to the performance of lignosulfonate. The di-methoxy reaction can increase active sites of lignosulfonate and carbonyl formation reaction can increase the molecular weight of lignosulfonate.

The HRPIB has good chemical and physical properties when lignosulfonate was grafted, by which lignosulfonate molecule changes the application performance. It is conducive to the development and utilization of lignosulfonate. For example, the decrement of glass transition temperature (T_g) reduces the surface polarity and increases the compatibility of lignosulfonate and non-polar polymer. Thus, the modified lignosulfonate can be used as an additive of plastic or rubber.

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