

Graft Copolymerization of Natural Rubber with Maleoyl Chitosan for Antibiosis

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Abstract—Elastomers are necessary materials in building materials. Mouldy materials will not only influence the surface view but also mechanical properties. In this paper, maleoyl chitosan (MCS) was selected as antimicrobial for improving natural rubber (NR) materials' antimicrobial properties together with mechanical and ageing properties. The results demonstrated that MCS showed antimicrobial effects and it also reinforced NR materials in mechanical properties. MCS is of good oil resistivity and thermostability. The copolymerization of them can not only improve the oil resistivity and thermostability of the natural rubber, but also can increase its medicinal value. Benzoyl peroxide (BPO), tert-butyl hydroperoxide (TBHP), dipotassium sulfonatoxy sulfate ($K_2S_2O_8$), azobisisobutyro-nitrile (AIBN), vulcanizing system (sulphur) were selected as initiators. A novel NR-MCS copolymer with much better mechanical property and antibacterial property was obtained at last which would be a good health and medical materials in the future.

Keywords-natural rubber; graft copolymerization; maleoyl chitosan

I. INTRODUCTION

Elastomers are necessary materials in building materials due to its splice and shockproof functions. Mouldy materials will not only influence the surface view but also mechanical properties. Natural rubber (NR) is got from the plant that can produce rubber latex. It is of excellent chemical and physical properties and can be widely used in many fields, such as: aerospace, war industry, tyre, medical elastomer. Medical elastomer has been used in medical care since the earlier 19th century. The medical elastomer must satisfy the same condition and reach the same goal: it can't hurt the health of the patient and the property must meet the requirement of the application. NR is the first elastomer used in medical care. However, its weak oil resistivity and thermostability restrict its application range.

Chitin is stored richly in the shells of ocean animals such as: shrimp, crab, shellfish and so on. The annual yield of the chitin is about ten billion tons which is just less than that of cellulose. However, chitin is insoluble in most of the solvent, which restrict its application enormously. Chitosan, which is made from the deacetylation of chitin, can be dissolved in the dilute acid. There are much more hydroxyl groups and amino groups in chitosan and it is easy for its structure to be decorated. Chitosan and its derivative are innocuous, biocompatible and biodegradable and can be widely used in biomedical, food, agriculture, cosmetics and environmental protection.

Maleoyl chitosan, which is made from the acylation of chitosan with maleic anhydride using sodium carbonate as catalyst, is a water-soluble polyelectrolyte with good heat resistance. We prepare the grafted copolymer of natural rubber and maleoyl chitosan to improve the oil resistivity and thermostability of the natural rubber. On the other hand, the chitosan is of special physiological and chemical properties, such as: innocuity, good biocompatibility and biodegradability. It also has kinds of pharmacological activities. Therefore, the copolymerization of natural rubber and Maleoyl chitosan may produce a novel polymer material with good medical and pharmacological value.

NR can react with many unsaturated compounds. The reaction of it with maleic anhydride is the earliest and most valuable. Bacon and Farmer found that plasticated NR and maleic anhydride can react in the benzene or toluene using benzoperoxide (BPO) as an initiator at 100°C for several hours and got white or buff larinoid product in 1939 [1]. Jia Demin grafted the natural rubber latex with maleic anhydride using BPO as an initiator [2, 3]. On the other hand, Zhang Jiping et. al studied on the preparation of maleoyl chitosan and used it as raw material of cosmetics [4]. There are also several other researchers prepared maleoyl chitosan with different methods [5-7]. Li Yongzhen et al.

prepared composite of maleoyl chitosan sodium and nano silica and found that its thermos stability improved strongly [8].

II. EXPERIMENT

A. Preparation of Maleoyl Chitosan in Water Medium

3.0g chitosan mixed uniformly with 300mL water at room temperature under stirring, then 1.0g sodium carbonate was added. Half an hour later, a certain amount of maleic anhydride was put into the mixture. Six hours later, the reaction was terminated by stopping stirring and 2.0 mol/L potassium hydroxide solution was added till the pH value of mixed solution to 10. High speed centrifugation was used to separate the rest chitosan from the solution. Hydrochloric acid was added to adjust the pH value of the supernatant clear liquid after centrifugation. When the pH value reach to 3.0, large quantity of white floc was precipitated and separated from the solution by centrifugation again. Then acetone was used to wash the powder until there is no precipitation while silver nitrate solution was added to the washings. The powder was dried *in vacuo* for 24 hours to get MCS.

B. Copolymerization of NR and MCS

0.5g MCS was solved in 50mL 10% (wt %) ammonia. The solution was drop wised into concentrated natural rubber latex (content of natural rubber is about 60%,wt%). Initiator was added in the mixture and the copolymerization happened under proper temperature. After suit time, the mixture after reaction was coagulated with the adding of NaCl. Then the coagulation products were washed with NaOH solution and water separately. Benzoyl peroxide (BPO), tert-butyl hydroperoxide (TBHP), dipotassium sulfonatoxy sulfate ($K_2S_2O_8$), azobisisobutyro- nitrile (AIBN), vulcanizing system (sulphur) (VS) were used as initiators.

TABLE I. INITIATION REACTION CONDITIONS

Initiator	KPS	TBHP	BPO	AIBN	VS
Reaction temperature/[°C]	60	60	80	80	60

III. RESULTS AND DISCUSSIONS

A. Preparation of MCS

MCS was prepared from the acylation of maleic anhydride with the amino group of the chitosan. He Jidong gave a hypothetical reaction route of the reaction, but the C6-OH is less reactive than amino group. We modify the ratio of MA and CS to control the graft ratio of MA onto the CS and restrain the esterification between MA and CS. The ideal graft copolymer to make amphiprotic polyelectrolyte is the MCS whose graft ratio on amino group is about 50%. Then the ratio of amino group and carboxyl group will be 1:1 in the MCS molecular. The main reaction route can be described as in Fig.1.

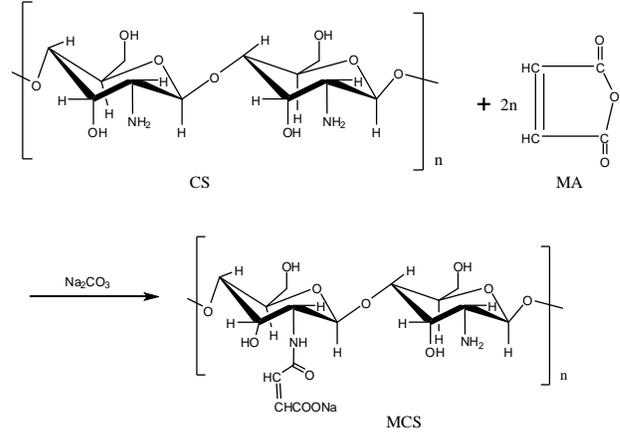


Figure 1. The reaction route of preparing MCS

To get the MCS with graft ratio near 50%, we investigated the relationship between feed ratio of CS to MA and graft ratio. The C percent and N percent were also tested to calculate the graft ratio.

TABLE II. THE RATIO OF MA TO CS AFFECTED TO THE REACTION

$M_{MA}: M_{CS}$	Yield/%	Graft ratio/%	C percent/%	N percent/%
1:3	10.83	23.82	44.08	7.39
1:2	17.05	37.51	44.56	6.93
1:1	23.28	43.77	44.83	6.75
2:1	41.25	50.30	45.12	6.57
5:2	45.27	58.62	45.61	6.38

The yield can be estimated from the weight of MCS (W_r) and the weight of MCS we can get from academic complete reaction (W_a). Suppose the reaction just happened between carboxyl group of MA and the amino group and there was only one carboxyl group of MA join the reaction.

$$\text{Yield}/\% = \frac{W_r}{W_a} \times 100\% \quad (1-1) \quad (1)$$

From the result, we can see the yield is not so high. The possible reason to explain this may come from the purification process of the MCS. MCS can dissolve in both alkaline and acid aqueous solutions while the CS can only dissolve in the acid aqueous solution. We can separate MCS from the residual CS by their different solubility in alkaline aqueous solution. As some of the MCS with low graft ratio can't dissolve in the alkaline aqueous solution completely, they are also removed, so the yield of the reaction may be lower. However, we can make sure that there is no CS in MCS, though the yield is low.

The graft ratio is calculated from the ratio of C content to N content (C/N) which is got from the elementary analysis result. Suppose the MCS is composed of ideal molecules which have no ester function and no cross linkage. The ratio of C content to N content (C/N) can be expressed by the graft ratio(x) in formula (1-2).

$$C/N = \frac{72 + 48x}{14} \quad (2)$$

$$x = \frac{72 - 14 \cdot C/N}{48} \quad (3)$$

B. FTIR Characterization of MCS

The FTIR spectra of CS and MCS give us 3 evidences for the acylation of CS and MA. First, the peaks at 1599cm⁻¹ and 1657cm⁻¹ which belong to free amino groups in FTIR spectra of CS move to 1559cm⁻¹ and 1623cm⁻¹ respectively which can confirm amide MCS. Second, the wide peak at about 3400cm⁻¹ which comes from the hydrogen bond caused by free amino groups and hydroxyl in CS become sharper and narrower in MCS. That would be the result of the increase of free amino group. Third, the peak at 3074cm⁻¹ and 842cm⁻¹ belong to the C=C bond of MA. As the MA has been completely removed from MCS, so the C=C bond has been introduced to the MCS molecular successfully. The peak at 1078 cm⁻¹ is the C-O of C₆-OH, which can be a proof that most of the C₆-OH still exist in MCS.

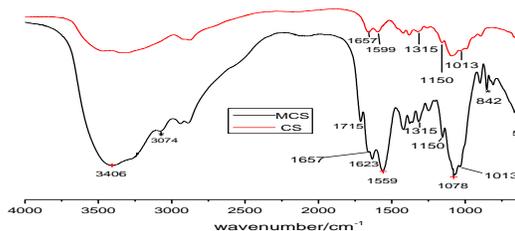


Figure 2. FTIR spectra of CS and MCS

C. FTIR Characterization of the Copolymers

Compared the FTIR spectra of the copolymers with the standard spectrum of natural rubber, some new peaks appear in the spectra except most of the absorption peaks in natural rubber. The FTIR absorption peak at 1542cm⁻¹ is the most obvious. This peak comes from flexural vibration of δN-H in MCS. This would be a good proof to the copolymerization of NR and MCS.

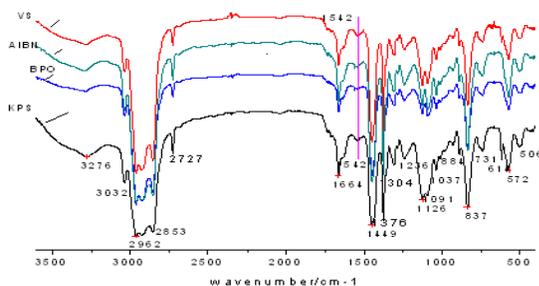
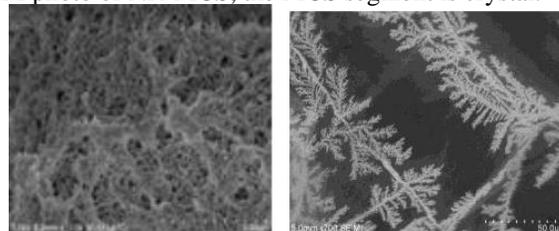


Figure 3. FTIR spectra of the NR-MCS copolymers

D. Micro Structure Observation

From the SEM photo of MCS, we can see that the state of MCS is amorphous. As prepared in water suspension, MCS has plenty of holes about μm degree. While in the SEM photo of NR-MCS, the MCS segment is crystal.



(a) MCS (b) NR-MCS
Figure 4. SEM photos of MCS and NR-MCS

E. Mechanical Property Test

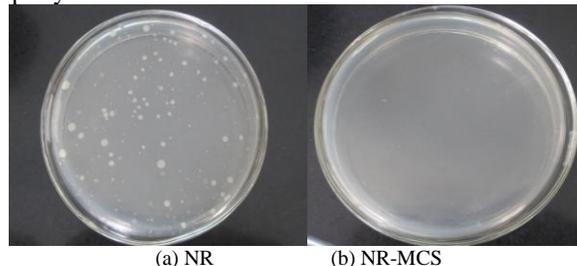
TABLE III. MECHANICAL PROPERTY TEST RESULTS OF NR-MCS COPOLYMERS

	Tensile strength /Mpa	Stress at 100%/MPa	Stress at 300%/MPa	Stress at 700%/MPa	Elongation at break/%
VS	41.025	0.8516	1.451	15.310	872.312
BPO	0.3405	0.252	0.287	0.224	1028.620
TBHP	2.245	0.582	0.835	1.531	963.025
KPS	0.431	0.344	0.385	0.412	821.667
AIBN	0.508	0.371	0.389	0.486	832.865

The NR-MCS from the initiation of vulcanizing system (sulphur) shows best compositive mechanical property which is much better than that of vulcanized NR. While the copolymers initiated by the other initiators possess even much lower mechanical properties than unmodified NR.

F. Antibacterial Property Test

From the photos of the washing water antibacterial test samples, there are plenty of bacteria groups grows in the washing water of NR after 48hours of the washing, while no group of bacteria grows in the washing water of NR-MCS. We can say that NR-MCS shows a much better antibacterial property than the NR.



(a) NR (b) NR-MCS
Figure 5. Photos of washing water of NR and NR-MCS after 48-hour test

IV. CONCLUSIONS

Acylation of chitosan with maleic anhydride mostly happens between the carboxyl group of MA and the amino group of CS. A novel NR-MCS copolymer is prepared with several initiators. The NR-MCS with vulcanizing system (sulphur) as an initiator shows a much better mechanical property than vulcanized NR from vulcanizing system (sulphur), while other NR-MCS copolymers possess an even worse property than NR. All the copolymers have a good antibacterial property.

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