

Preparation of NR/SBR Blends and Their Biopolymeric Derivatives For Water Treatment Usage Via Different Sulfur Curing Systems

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ABSTRACT

Compared to other synthetic rubbers, natural rubber (NR) has relatively good eco-friendly properties which provides itself the great potentials in environmentally restricted areas. In this study, the natural rubber that applied in water purification industry was blended with styrene-butadiene rubber (SBR) to overcome its inherent shortages. To understand the relationship between curing system/sulfur-accelerant ratio and mechanical properties of vulcanizates, NR and SBR were physically mixed with different formulations under two-roll mixing mill, and examined vulcanization characteristics of the compound. Then we prepared a series of NR/SBR vulcanized rubbers via conventional vulcanization (CV), effective vulcanization (EV) and semi-effective vulcanization (SEV) respectively basing on each formulation and optimum curing time. We examined the mechanical properties of NR/SBR vulcanizates including tensile strength, tear strength, elongation at break, modulus, Shore A hardness and relative volume abrasion. The results indicated that NR/SBR vulcanizates prepared in different systems differed in mechanical properties. Vulcanizates prepared via CV showed higher tensile and tear strength; vulcanizates prepared via EV had high modulus and hardness, and vulcanizates prepared via SEV performed high abrasion resistance. In the CV system, sulfur-accelerant ratio affected the mechanical properties. As the sulfur-accelerant ratio increased from 2.92 to 3.75, the strength of tensile and tear, elongation at break of vulcanizates increased at first then decreased, while the modulus and Shore A hardness increased. The Relative volume abrasion decreased at first and then increased. In the EV system, sulfur-accelerant ratio also showed to affect the mechanical properties. As the sulfur-accelerant ratio increased from 0.2 to 0.42, the tensile strength and tear strength increased, the elongation at break decreased, and the rebound resilience and Relative volume abrasion maintained at a range. The strength modulus and Shore A hardness changed irregularly. Compared to CV and EV, in SEV system that the sulfur-accelerant ratio was 1.14, the abrasion resistance of vulcanizates was significantly improved, but the strength and hardness was improved slightly. The Relative volume abrasion reached 173mm³. The other mechanical properties of vulcanizates from SEV system were between the CV and EV. The results from our study demonstrated that both vulcanization system and sulfur-accelerant ratio can affect the mechanical properties, and the CV can provide vulcanizates better mechanical properties. In addition, the NR/SBR vulcanizates provided a homogeneous phase, and the vulcanizates with different curing systems were stable in water environment up to 90 days. In addition, the biopolymeric chitosan derivatives were synthesized and physically introduced into the blends to provide water treatment functions.

Key words: sulfur-accelerant ratio, stress concentration, crosslink bond, crosslink density

1 Introduction

Natural rubber (NR polyisoprene), as mainly harvested from natural products, possesses relatively good eco-friendly properties compared to other synthetic rubbers^[1], therefore NR has been used in some environmentally restricted areas. To overcome its inherent shortages, NR has been widely blended with styrene-butadiene rubber (SBR). NR/SBR combines the advantages of NR and SBR and possess fine comprehensive qualities so that it could be practically used in some specific fields (e.g. water treatment industry)^[1,2]. Currently, many NR/SBR vulcanizates are being used in dynamic environments, which require NR/SBR with fine mechanical properties in both static and dynamic state^[2]. Thus, examinations and analysis of the comprehensive mechanical properties of NR/SBR are necessary before their industrial application.

Researches have demonstrated curing system directly affected on vulcanizates' mechanical properties besides constituents' structures and characteristics^[3-13]. Curing system is always concerned because it can directly alerts vulcanizates' structures as well as affects vulcanizates' dynamical mechanical behaviors, and further determining mechanical properties^[10-13]. In most cases, sulfur curing systems were used to prepare NR/SBR vulcanizates^[2]. According to the constituents' ratio of curing systems, there are three kinds of curing systems: conventional vulcanization (CV), effective vulcanization (EV) and semi-effective vulcanization (SEV)^[2]. The most significant difference among these three systems is the sulfur-accelerant ratio (it means the ration of the amount of sulfur and the amount of accelerant). The sulfur-accelerant ratio is usually higher than 2.5 in CV, while the sulfur-accelerant ratio in EV is usually less than 0.4 and the sulfur-accelerant ratio is nearly equal to 1 in SEV. The difference in sulfur-accelerant ratio affects the type of crosslink bond and crosslink density of vulcanizates, consequently affects the vulcanizates' configuration, regularity, and crystallization or orientation behaviors, and will finally determine vulcanizates' mechanical properties. Thus, screening appropriate curing system is critical in a given environment. Some researches reported that CV system is suitable for vulcanizates in dynamic environment and EV system is good for that in static environment with high temperature^[14-19]. However, these experiences didn't comparatively test the effects brought by curing systems and the sulfur-accelerant ratios on vulcanizates.

Therefore, in this study, the NR that used in water treatment application was selected for blending with SBR, and biopolymeric derivatives were introduced to provide bio-activities for water treatment usage. The NR/SBR was vulcanized via conventional vulcanization (CV), effective vulcanization (EV) and semi-effective vulcanization (SEV) systems respectively. In the following test, we then examined the mechanical properties of the prepared NR/SBR vulcanizates. These mechanical properties include tensile strength, tear strength, elongation at break, modulus, Shore A hardness and relative volume abrasion.

2. Experiment Section

2.1 Materials and instruments

The compound formulation for preparing NR/SBR under the three curing systems was indicated in Table 1.

Table .1 Compound formulations for the three curing systems (unit: g)

Compounds added	CV	EV	SEV
NR	180	180	180
BR	120	120	120
HAF	150	150	150
Silica	75	75	75
Oil	75	75	75
ZnO	15	15	15
Stearic acid	6	6	6
Paraffin	3	3	3
CZ	3	3	3
4010NA	3	3	3
TMTD	0.6	2.7-4.5	1.8
Precipitated CaCO ₃	30	30	30
S	10.5-13.5	1.5-2.4	4.2

The devices used in our study were two roll rubber mixing mill (Shanghai Institute of Mechanical Technology), rotorless curemeters (GT-M2000-A, GOTECH CO LTD, Taiwan), Daylight press (Jiaxin Electric Device Technology CO LTD), electronic tensile testing machines, Shaore A durometer, rotating cylindrical drum device (GT-7012-D, GOTECH CO LTD, Taiwan) and densimeter (Preciso CO LTD).

2.2 The preparation of NR/SBR vulcanizates

We prepared the NR/SBR compound basing on ISO 2393:2008 and prepared NR/SBR vulcanizates basing on ISO 3417:1991. Examination of curing property was based on ISO 6502:1991. Temperature and pressure for preparing vulcanizing were 145 °C and 10 MPa respectively. Optimum curing time was obtained from the curing curve (Table 2). After preparation, the morphologies of NR/SBR vulcanizates were investigated by scanning electron microscopy (SEM). To prepared the corresponding biopolymeric products, the chitosan derivatives (include the schiff base and self-assembly particles) were used as bio-additives (with 5% wt addition) in the blends (see supportive information).

2.3 Examination of NR/SBR vulcanizates

We measured tensile strength basing on ISO 37: 2005, and tear strength basing on ISO 34-1:1994, rebound resilience basing on ISO 4662-1986, modulus and elongation at break basing on ISO 37:2005, Shore A hardness basing on to ISO 7619-1:2004, relative volume abrasion basing on the ISO 4649: 2002 and density basing on the ISO 2781:2007. The water stability tests were conducted based on a previous report^[6].

Table 2 Curing time for each vulcanizates in given sulfur-accelarantrations

Treatment No.	s/a	Optimum curing time
1	3.75	6'44"

2	3.33	7'41"
3	2.92	6'15"
4	1.14	5'06"
5	0.42	7'00"
6	0.36	9'55"
7	0.2	10'18"

3. Results and Discussion

The results from our study showed that vulcanizates prepared via CV had higher tensile and higher tear strength, while vulcanizates prepared by EV had high modulus and hardness, and vulcanizates prepared through SEV possessed high abrasion resistance (Table 3 and 4). In our study, the differences of mechanical properties were mainly caused by the differences of crosslink bonds and crosslink density among the three curing systems. The processing techniques also resulted into these differences.

Table 3 Experiment record of mechanical properties under CV

Parameters tested	Vulcanizates		
	1 (s/a=3.75)	2 (s/a=3.33)	3 (s/a=2.92)
Tensile strength/MPa	16.8	17.2	16.6
Tear strength/kN*m ⁻¹	35.0	37.9	36.5
Elongation at break/%	361	379	344
Modulus (100% elongation)/MPa	3.5	3.3	3.3
Modulus (200% elongation)/MPa	8.3	7.8	7.5
Modulus (300% elongation)/MPa	-	11.2	11.4
Rebound resilience/% compression set	60	60	61
Shore A hardness	64	67	62
Relative volume abrasion /mm ³	202	207	213

Table 4 Experiment record of mechanical properties under EV/SEV

Parameters tested	Vulcanizates			
	4 (s/a=1.14)	5 (s/a=0.42)	6 (s/a=0.36)	7 (s/a=0.2)
Tensile strength /MPa	15.2	14.8	14.2	13.7
Tear strength /kN*m	35	33.7	32.5	30.9
Elongation at break/%	380	358	387	423

Modulus (300% elongation)/MPa	14.2	13.7	12.7	12.8
Rebound resilience/%	58	58.5	59	57
Shaore hardness	68	72	73	70
Relative volume abrasion /mm ³	173	221	222	217

3.1 Crosslink bond type and its effects on vulcanizates' mechanical behaviors

Stress-strain behaviors. In sulfur curing system there are three main types of crosslink bond: polysulfur bond (usually existing in CV), disulfide bond and monosulfur bond (both usually exist in EV/SEV and monosulfur bonds usually existing in SEV). Among the three types of bonds, the bond energy of polysulfur bond is relative lower ^[2] (Table.5), resulting in a flexible bond. Thus, when stress concentration effect appears, flexible polysulfur bond can change shape and the chain gets enough time to orient and crystallize. This relative lower bond energy also makes polysulfur bonds easy to break down and rearranged. Therefore, the stress concentration effect can be weakened. Meanwhile, energy was absorbed so that dynamic loss was reduced during the rearrangement process. Disulfide bond and monosulfur bond, however, are usually short and rigid. These kinds of bonds tend to break down rapidly under stress and there is little time for the chain to orient and crystallize. Also, most disulfide bonds and monosulfur bonds are chemical inert. They cannot rearrange after broken, resulting in a lower integrated strength. Thus, vulcanizates with more polysulfur bonds have better strength in general.

Table 5 Common crosslink bond type and bond energy

Crosslink bond type	Curing systems	Bond energy/kJ.mol ⁻¹
Monosulfur bond	EV/SEV	284.7
Disulfide bond	EV/SEV	267.9
Polysulfur bond	CV	<265

Stress relaxation behaviors. The modulus and hardness usually were affected by stress relaxation behaviors. In our experiment, modulus and hardness were higher under EV (Table 3-4) that was induced by difference rates of stress relaxation in each vulcanizate. Here we used Parallel Maxwell Model ^[20] to explain why there are differences in stress relaxation behaviors among the three curing system. The stress relaxation formula was as follow ^[21]:

$$\sigma = \sum_i \sigma_{0i} e^{\frac{-t}{\tau_i}} \quad E = \sum_i \frac{\sigma_{0i}}{\varepsilon_0} e^{\frac{-t}{\tau_i}}$$

In these formulae, σ_{0i} represents each Maxwell unit's stress, τ_i represents each unit's relaxation time and E represents the Young's modulus. As mentioned above, polysulfur bonds are easier to change shape and rearrange. Therefore, flexible polysulfur bonds make vulcanizates' stress relaxation rate in CV system faster than that in EV and SEV. This means in CV system, τ_i is generally short and the modulus (hardness) is low. By

contrast, disulfide bonds and monosulfur bonds can slow down the vulcanizates' stress relaxation rate and prolong the τ_i so that modulus and hardness were higher under EV.

Dynamic abrasion behaviors. Vulcanizates' abrasion behaviors include wear abrasion, fatigue abrasion and curl abrasion. All of those are related to the mechano-chemical active chain-oxydized reaction initiated by stress [22]. During the reaction, the chain and crosslink bonds will be broken down and form ether bonds [23]. Jia reported that the degree of abrasion is in direct proportion to the amount of crosslink bonds broken down in the vulcanizates [23]. Table 5 showed that among three types of bonds, monosulfur bond possesses highest bond energy so that it is not easy to be broken down in stress. Based on this, we suggested that in the same condition, vulcanizates prepared in SEV possess better abrasion resistance properties.

3.2 Crosslink density and its effects on vulcanizates' mechanical properties

From the Table 3 and Table 4, we found that the sulfur-accelerant ratio was influential on mechanical properties in each curing system. In the CV system, as the sulfur-accelerant ratio increased, the strength of tensile and tear, elongation at break of vulcanizates increased at first, reached the maximum and then decreased, while the modulus and Shore A hardness increased (except in 300% elongation). The Relative volume abrasion decreased at first and then increased. In the EV system, as the sulfur-accelerant ratio, the tensile strength and tear strength increased, the elongation at break decreased, and the rebound resilience and Relative volume abrasion maintained at a range. The strength modulus and Shore A hardness changed irregularly. Compared to that in CV and EV, product from SEV system possessed intermediate mechanical properties of vulcanizate.

Different sulfur-accelerant ratio impacts various crosslink densities. In sulfur curing system, crosslink density can affect vulcanizates' behaviors in both static and dynamic state. With the crosslink density increasing, vulcanizates may become three-dimensional and chain segments may have to overcome more constraints to move. Usually, the modulus, hardness, strength and elongation increase with the crosslink density increasing,. However, we found that when crosslink density reached a certain value the modulus, hardness, strength and elongation did not increase with the crosslink density increasing. This phenomenon can be explained by NR's crystallize and orientate behaviors.

Crystallize behaviors. The Avrami formula often explains crystallize behaviors [21]. The Avrami formula indicates as follow.

$$X_{c,t}^V = X_{c,\infty}^V (1 - e^{-kt^n}),$$

X represented the degree of crystallinity of NR. k is the crystallization rate constant. t is the crystallization and n is Avrami index. In our systems, we did not add any crystallization agents. Therefore, we could assume that the crystal nucleus formed homogeneously, and the main crystal structures were oblique crystal. The n value thus can be a constant as 4 in this system [21]. Under this circumstance, only the t and k determines the degree of crystallinity. When crosslink density is beyond a certain range, the space for crystallization is

replaced by extra crosslink bonds and k will become smaller. And the time for NR to get crystallized under stress will be longer. Then the degree of crystallinity will be reduced, which further reduces strength.

Orientation behaviors: The orientation factor ($F=(3\cos^2\theta-1)/2$) represents degree of the orientation^[21], the θ is angle between direction of rubber's chain and direction of orientation. Usually in NR or SBR, the chains orient partially random. However, chains will orient in the same direct with stress, which means the θ will reach 0 (the F will reach 1). If crosslink density is too concentrated, orientation direction will be seriously interfered, the θ will be changed and F will become smaller than expected. Thus, the vulcanizates' strength can be weakened.

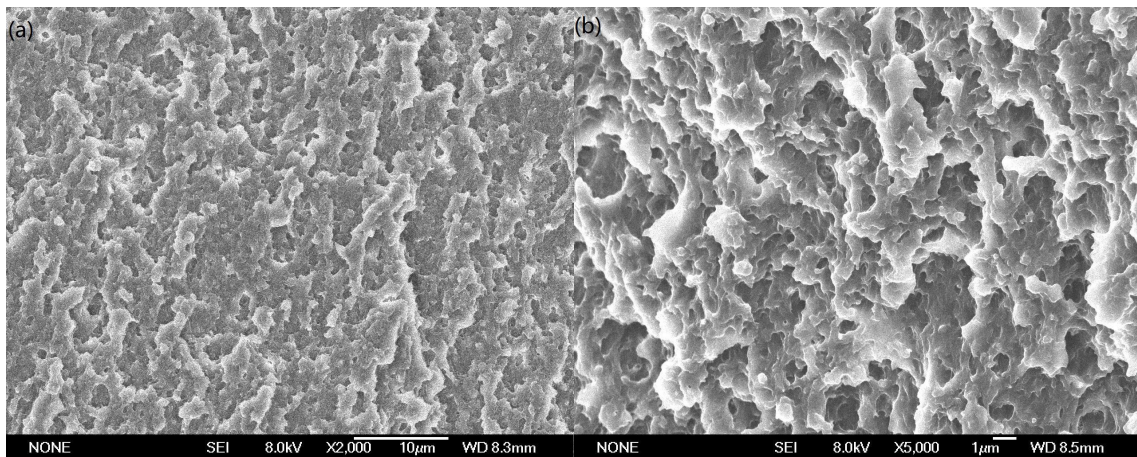
3.3 Vulcanization process techniques

Vulcanization process techniques including especially temperature and curing time often affect crosslink bonds and crosslink density. The curing time were obtained from the curing curve (Table 2). Considering the environment difference between laboratory and factory, we prolonged 5 extra minutes to optimum curing time. Usually the formation of crosslink bonds are dependent on the curing time, but if the vulcanizate is heated too long, crosslink bond will break down and rearrange, the chain also reacts with each other^[23]. Thus, the vulcanizate's appearance and qualities can be seriously affected. So, in our experiment, we set the time based on the theoretical curing time rather than optimum curing time.

Traditionally the temperature is set in the range from 143 °C (for NR) to 150 °C (for SBR)^[1,2]. In this work, we controlled the temperature at 145 °C \pm 0.5 °C. According to Van't Hoff formula^[2] and Arrhenius formula^[2], improving heating degree will shorten the curing time, but high temperature could lead vulcanizates chain breakdown and affect strength^[24]. So we did not set temperature over 150 °C (Table 2).

3.4 Morphologies characterization

As shown in figure 1, the SEM images displayed that the NR/SBR vulcanizates, despite prepared by different curing systems, possessed a homogeneous phase, which means the NR and SBR are compatible.



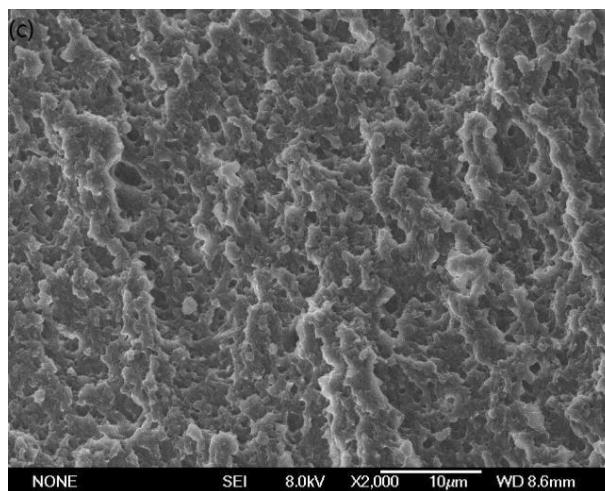


Fig 1. SEM images of NR/SBR vulcanizates prepared by CV (a), EV (b) and SEV (c) curing system.

3.5 Water stability test

Fig.2 showed the water stabilities of NR/SBR vancanizates. After 90 days of treatment the mass increment could reach up to 3.8% and the increment became ceased to would not continue. The results indicated that the NR/SBR vulcanizates were stable in aqueous environment and capable in water treatment industry.

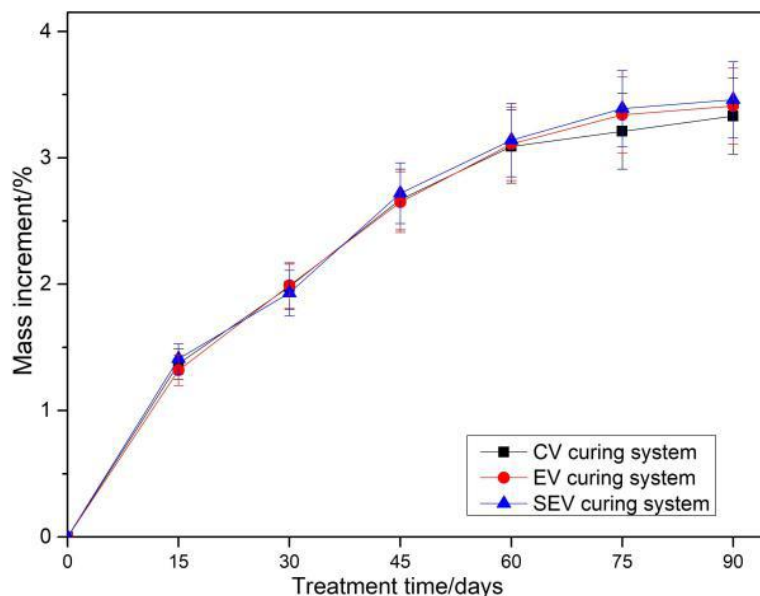


Fig.2 Water stability of NR/SBR vulcanizates

3.6 Incorporation of biopolymeric derivatives

The presence of chitosan in the derivatives could be confirmed by FT-IR subtraction spectra (shown in Fig.3), the peaks around 2900 cm^{-1} could be attributed to the alkyl groups from modified chitosan, peaks around 1050 cm^{-1} were related to the chitosan's cellulosic ring. The X-ray photoelectron spectroscopy (XPS) assessment also indicated the incorporation of chitosan derivatives as the nitrogen content (from the amino groups on chitosan) increased.

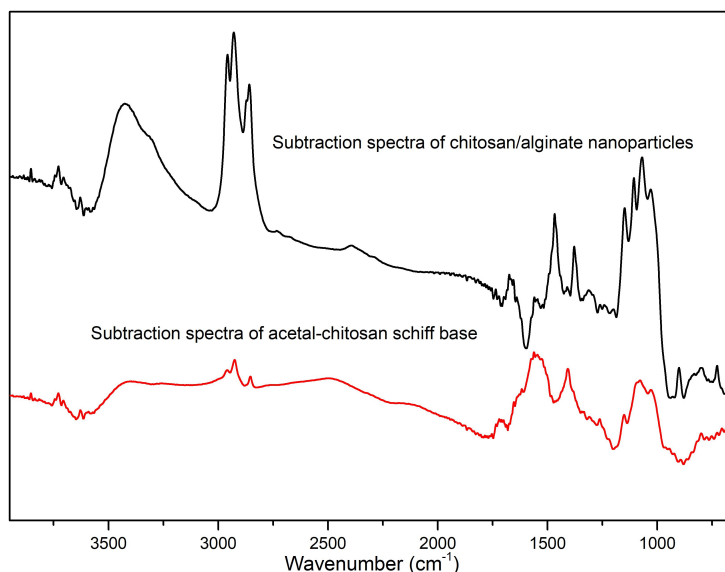


Fig.3 FT-IR subtraction spectra of chitosan incorporated NR/SBR blends (via SEV curing system)

Table 6 XPS test of nitrogen contents of NR/SBR blends (via SEV curing system)

	Nitrogen content (%wt)
NR/SBR	0.03
Acetal-chitosan schiff base incorporated NR/SBR	0.44
Chitosan/alginate incorporated NR/SBR	0.31

4. Conclusion

Curing system and the sulfur-accelerant ratio affected the mechanical properties of NR/SBR vulcanizates interactively. In our cases, CV can provide vulcanizates relative better strength, EV can provide vulcanizates relative better modulus and hardness, and SEV can provide better abrasion resistance. Our results indicated that mechanical properties of vulcanizates' varied non-linearly with the sulfur-accelerant ratio. There was an optimum value of sulfur-accelerant ratio for each mechanical property under the three curing systems. For CV system, optimum value of sulfur-accelerant ratio was 3.33, while for SEV/EV system, this ratio was 1.14. The results improve our understanding to the effects of sulfur-accelerant ratio on mechanical properties in different curing systems.

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Supporting information

Synthesis of chitosan based schiff base: 1g chitosan was dissolved into 100mL 1% (v/v) acetic acid (in the round bottom flask), after that 10 mL acetaldehyde was added into the chitosan solution. The reaction was performed under 70°C, regular pressure for 1 hour. After cooling down to the room temperature, 10% (w/v) sodium hydroxide solution was added to adjust the pH to 10. The precipitants were filtered and washed by ethanol and distill water until the pH reached at 7. Finally, the products were dried under 40°C.

Syntheiss of chitosan/alginate nanoparticles: 10 mg/mL alginate and chitosan solution were prepared at first. The chitosan solution was directly added into alginate solution with constant stirring (180 rpm) for 120 minutes at 4°C. After reaction, the solution was centrifuged at 3000 rpm for 10 minutes. The upper layer solution and filtered by 0.45 µm syringe filter, then the filtered solution was under dialysis for 24 hours to remove unreacted chitosan and alginate. The dialyzed solution was frozen in liquid nitrogen and then lyophilized for storage.