

琼枝多糖凝胶的结构和性质*

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提 要 本文研究琼枝多糖凝胶的结构和性质。大多数碱金属盐、碱土金属盐和含二个氨基以上的化合物能够改良这种带负电荷的多糖凝胶的性能。从扫描电子显微镜研究各种凝胶的结果看出,琼枝多糖象绞合的纤维束同方向地聚集;琼枝多糖-KCl凝胶象疏松绞合着的纤维束同方向聚集;琼枝多糖-乙二胺凝胶象多锁链同方向聚集;琼枝多糖-明胶凝胶却象海绵一样网状聚集。根据试验结果,作者对琼枝多糖形成凝胶的机理进行了推断。

关键词 琼枝、卡拉胶、带负电荷多糖凝胶、扫描电子显微镜

卡拉胶(Carrageenan)凝胶除广泛用于食品、医药和日用化工品外,近年来其应用有了新的进展,如作为固相酶的载体和固定化细胞的包埋材料,卡拉胶是性能最优良的一种^[2]。琼枝多糖是一种硫酸根含量较少、凝固点较高、凝胶强度也较高的卡拉胶,其物理性能类似琼胶(Agar)。为了开辟琼枝多糖的新用途,作者对琼枝多糖凝胶及其化学改性作了研究,发现多数碱金属盐和碱土金属盐以及含二个氨基以上的化合物都能改善琼枝多糖凝胶的性能,这为琼枝多糖的应用开拓了广阔的前景。

作者用扫描电子显微镜研究了多糖凝胶的结构,结合对凝胶性质的研究,阐明化学改良剂对琼枝多糖凝胶的作用,并对琼枝多糖形成凝胶的机理进行推断。

关于卡拉胶的形成凝胶机理,十多年来 Rees 等提出的双螺旋理论比较流行^[3,5-8]。1979年 Olav smidsrød 提出了与 Rees 观点不同的有序构象→选择离子盐桥两步形成凝胶的机理^[9,10]。尔后,Rees 等又根据新的证据对自己过去提出的模型作了修正,提出阳离子居中间的螺旋-螺旋聚集机理^[4]。上述学者已报告的仅限于金属阳离子促进成胶过程的讨论,没有涉及有机化合物和大分子化合物对卡拉胶的作用机理问题。

本文根据试验结果对金属阳离子、有机化合物和大分子化合物促进琼枝多糖形成凝胶的机理进行讨论。

材 料 和 方 法

(一)材料:琼枝多糖,从海南岛琼海沙薯人工养殖的琼枝(*Eucheuma gelatiniae*)分离制取^[1]。分子量 2.25×10^5 。明胶(gelatin),包头明胶厂生产,分子量 6.78×10^4 。

(二)试验方法:凝胶强度测定:将制成的凝胶于5°C放置5小时后,用直径为1.6cm的金属柱垂直作用于凝胶上,当凝胶破裂时,凝胶单位面积的负荷定为凝胶强度。脱水率测定:将凝胶置于-20°C冷冻24小时后,取出置于室温下融化脱水,测量脱水量,算出脱水率。扫描电子显微镜观察:将冷冻脱

* 扫描电子显微镜观察和照相由陈子灿协作进行,特此致谢。

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水后之凝胶用乙醇处理,切片,真空干燥后,在 HITACHI S-430 扫描电子显微镜上观察、照相。

结果与讨论

K^+ , Rb^+ , Cs^+ , Mg^{++} , Ca^{++} , Sr^{++} , NH_4^+ 等阳离子存在时,琼枝多糖凝胶的强度有较大幅度提高(见表 1),而且凝胶强度随阳离子的浓度增加而增加,至离子浓度达到一定值后,凝胶强度便随离子浓度的继续增加而降低。以 KCl 为例,在 3%(W/V)多糖凝胶中, KCl 浓度在 $7.5 \times 10^{-2}M$ 以下时,凝胶强度随 KCl 浓度的增加而迅速增加。当 KCl 浓度增至 $7.5 \times 10^{-2}M$ 以上时,凝胶强度便随 KCl 浓度的增加而下降,即凝胶强度与 KCl 浓度的关系曲线有一最高点(见图 1)。按照琼枝多糖的组成^[1]可算出这最高点是约二个半乳糖基和一个 KCl 分子形成的凝胶强度。

Li^+ 和 Na^+ 离子不能使琼枝多糖凝胶的强度提高(见表 1),说明琼枝多糖对阳离子有选择性。

表 1 不同阳离子存在时琼枝多糖凝胶强度

Table 1 The strength of polysaccharide gel from *Eucheuma gelatinae* in the presence of various cation

加入凝胶的阳离子	凝胶强度 g/cm ²	加入凝胶的阳离子	凝胶强度 g/cm ²
..	243.6	Mg^{++}	272.8
Li^+	239.6	Ca^{++}	347.2
Na^+	182.7	Sr^{++}	290.5
K^+	566.8	Ba^{++}	274.4
Rb^+	611.6	NH_4^+	391.3
Cs^+	374.6		

注:阳离子浓度:0.1M,多糖浓度:2%(W/V)

表 2 氨基化合物存在时琼枝多糖凝胶强度

Table 2 The strength of polysaccharide gel from *Eucheuma gelatinae* in the presence of amino-compound

氨基化合物	—	尿 素 $NH_2-CO-NH_2$	乙 二 胺 $NH_2-(CH_2)_2-NH_2$	赖 氨 酸 $(CH_2)_4-NH_2$ $NH_2-CH-COOH$	谷 氨 酸 $(CH_2)_4-COOH$ $NH_2-CH-COOH$
凝胶强度 g/cm ²	243.1	268.0	377.5	358.1	不能测量

注:氨基化合物浓度:0.1M,多糖浓度:2%(W/V)

尿素、乙二胺和碱性氨基酸(如赖氨酸)等含二个氨基以上的化合物能与琼枝多糖反应,使凝胶强度提高,而酸性氨基酸如谷氨酸却使凝胶强度降低(见表 2)。

明胶也能和琼枝多糖发生反应,生成琼枝多糖-明胶复合物,它是一种高强度弹性体,其凝胶强度比多糖或明胶本身高得多。明胶和琼枝多糖的重量比为 4:1 时,其凝胶强度最高(见图 2),按分子量计算,大约 1 个分子琼枝多糖与 12 个分子明胶所形成的复合物,凝胶强度最高。琼枝多糖-明胶复合物可进一步与甲醛起反应,生成凝胶强度更高的交联

产物,而金属盐和乙二胺却使复合物凝胶强度降低(见表 3)。

从测得的各种凝胶的脱水率(见表 4)可看出, K^+ 离子使多糖凝胶变得易于脱水,而乙二胺和明胶却使多糖难于脱水。其脱水容易程度的顺序如下:

多糖- K^+ > 多糖 > 多糖-明胶 > 多糖-乙二胺

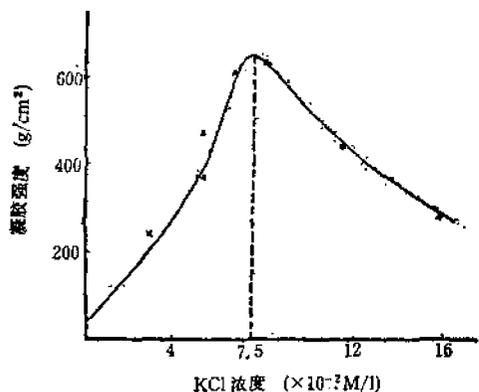


图 1 凝胶强度与 KCl 浓度关系曲线

Fig. 1 The relative curve of gel strength-concentration of KCl

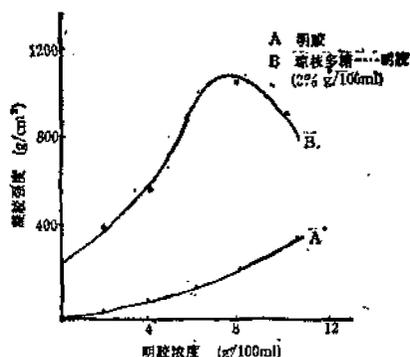


图 2 凝胶强度与胶浓度关系曲线

Fig. 2 The relative curve of gel strength-concentration of gel

表 3 各种添加物对琼枝多糖明胶-凝胶强度的影响

Table 3 The effect of various additives on gel strength

添加物	凝胶强度(g/cm ²)	添加物	凝胶强度(g/cm ²)
—	1045	氯化钾	872.8
甲醛	2818	乙二胺	682.8

注: 琼枝多糖浓度 2%(W/V), 明胶浓度 6%(W/V), 添加物浓度 0.1M

表 4 各种凝胶的脱水率

Table 4 The dewatering rate of various gel

凝胶	琼枝多糖	琼枝多糖-KCl	琼枝多糖-乙二胺	琼枝多糖-明胶
脱水率%	39	63	12	23

通过电子显微镜扫描观察凝胶的构造(照片 1~4), 可看出琼枝多糖凝胶像绞合的纤维束同方向聚集; 琼枝多糖-KCl 凝胶像疏松地胶合着的纤维束同方向聚集, 但其“纤维束”比琼枝多糖粗得多, 绞合程度也疏松得多; 琼枝多糖-乙二胺像很多锁链同方向聚集; 琼枝多糖-明胶却像海绵一样网状聚集。从它们聚集的有序程度和紧密程度可以说明凝胶强度大小和脱水的难易程度。琼枝多糖-KCl 凝胶的聚集比琼枝多糖本身规整, 且聚集比较疏松, 因此凝胶强度比多糖本身高, 而脱水比较容易; 琼枝多糖-乙二胺和琼枝多糖-明胶聚集比多糖本身紧密, 因此凝胶强度较高, 脱水也较难, 琼枝多糖-明胶尤为甚之。

从以上结果, 可以认为 K^+ 对琼枝多糖的作用机理与乙二胺和明胶的作用机理不同,

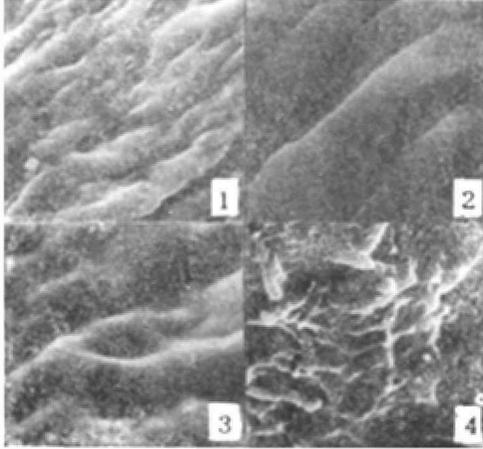


图3 各种凝胶的扫描电子显微镜照片
Fig. 3 The scanning electron microscope photo of various gel.

1. 琼枝多糖 2. 琼枝多糖-KCl 3. 琼枝多糖-乙二醇 4. 琼枝多糖-明胶

可以作如下推断:

(一) 由于多糖分子是半乳糖硫酸酯基和 3, 6-内醚半乳糖基假重复交替连接而成, 具有不对称性。当溶胶冷却时, 分子的布朗运动减弱, 不对称胶团发生有序变化, 即胶团产生定向化, 而且邻近分子链段间产生氢键合而形成有序的三度空间框架结构, 凝聚成凝胶。

(二) 加入 K^+ 时, 由于阳离子的水合作用, 使多糖胶团部分失水。同时, 带正电的阳离子使带负电的胶团荷电中和, 因而相互间更加靠近并更加有序地聚集, 同时 K^+ 在大分子胶团间起着“选择盐桥”作用, 其结合力比氢键合强。

(三) 当加入乙二醇等含二个氨基的化合物时, 氨基与多糖中的 $-OSO_3-$ 基反应,

生成胺盐⁽¹⁾而成网状结构, 凝聚成胶。

(四) 加入明胶时, 明胶中的 $-NH_2$ 基与多糖中的 $-OSO_3-$ 基反应也生成胺盐, 形成两种大分子间紧密交联的网状结构而成凝胶。

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STRUCTURES AND PROPERTIES OF POLYSACCHARIDE GEL FROM *EUCHEUMA GELATINAE*

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ABSTRACT The structures and properties of polysaccharide from *Eucheuma gelatinae* were studied, and according to the results of experiment, the gelation mechanism was deduced.

The polysaccharide gel in the presence of K^+ , Rb^+ , Cs^+ , Mg^{++} , Ca^{++} , Sr^{++} , Ba^{++} and NH_4^+ forms gel which has higher strength than the original. The strength of gel increases with concentration of adding salt, and it attains the maximum value as the ratio of cation number to galactose residue is 1:2, and then starts decreasing. The polysaccharide reacted with compounds contain two amino-groups such as urea, alkaline amino-acid and ethylenediamine to form higher strength gel.

The polysaccharide also reacted with gelatin to form complex which was a high strength elastomer. The complex could react with the formaldehyde to form a very high strength gel. Its strength was about twice as that of the original complex gel.

The scanning electron microscope revealed that the shape and aggregating compactness of section of gel after freeze-drying agree with the order of dehydrating tendency. From above results, it may be considered that the reaction mechanism of cation on the polysaccharide was different from that of diamine and gelatin.

The research into various polysaccharide gel by scanning electron microscope indicated that the polysaccharide gel was like the sparse twisting fiber cluster and aggregated each other in a same direction; the polysaccharide-KOI was like the untwisting fiber cluster, and aggregated in a same direction; the polysaccharide ethylene diamine was like some chains aggregating in a same direction; and polysaccharide-gelatin was like sponge.

According to above evidence, the gelation mechanism was deduced as follows.

1) When the temperature of polysaccharide sol-gel lows, the Brownian movement of molecules is weakened. In addition, the polysaccharide molecule exhibits asymmetry because it is alternately linear comprised by galactose residues and 3,6-anhydro-D-galactose residues, with repeated structure. The neighbor molecule segments were held together regularly to form a three dimensional framework by

hydrogen bonds.

2) The polysaccharide gel particles, in presence of cation (K^+), dehydrated due to the hydration of cation. In addition, the negatively charged gel particles were neutralized by cation. Then the macromolecule gel particles further approaches to each other, and regularly associated to develop a cohesive network by cation "salt bridges".

3) In case of adding the compound which contain two amino-groups such as ethylenediamine, the amino-groups of the compound reacted with sulfate groups in the polysaccharide to form amino-group salts, crosslinking to network structure.

4) In case that gelatin was added, multiple amino-groups in gelation reacted with sulfate groups in the polysaccharide to form amino salts and develop a cohesive network involved both macromolecules.

KEYWORDS *Eucheuma gelatinae*, carrageenan, negatively charged polysaccharide gel, scanning electron microscopy

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用主机相同功率的目的。我们在 ZCY207 型渔船上所进行的试验,在国内还是首次尝试,为我国渔船在船一机一桨的匹配设计中,增添了一种新的设计方法。在我国渔船更新换代中,它将以良好的经济收益,得到广泛的应用。

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