Mar. Üniv. Ecz. Der.,
2 (1), 47—55 (1986)

J. Pharm. Univ. Mar.,
2 (1), 47—55 (1986)

GÖKÇEADA'DAN (EGE DENİZİ) TOPLANAN CYSTOSEIRA CORNICULATA VE CAPOMENIA SINUOSA'DAN ELDE EDİLEN SODYUM ALGİNATLARIN REOLOJİLERİ

RHEOLOGY OF SODIUM ALGINATE IN CYSTOSEIRA CORNICULATA AND CAPOMENIA SINUOSA FROM GÖKCEADA IN THE AEGEAN SEA

İsmail PEKER *

SUMMARY

Cystoseira corniculata and *Colpemenia sinuosa* were collected from Gökceada shores and sodium alginate was prepared from these seaweeds. Rheological studies were carried out under conditions of varying temperature and concentration. It was found that sodium alginate from *C. corniculata,* shows typical preudoplastic behaviour but this was not apparent in that from *C. sinuosa*. Temperature has an effect on the apparent viscosity of sodium alginates from these brown seeweeds at lower rather than higher shear rates.

ÖZET

C. corniculata ve *C. sinuosa* Gökceada kıyılarından toplanarak bu yosunlardan sodyum alginat elde edildi. Reolojik çalışmalar değişik temperatür ve konsantrasyonlarda gerçekleştirildi. *C. corniculata*'dan elde edilen sodyum alginatın tipik psödoplastik akış özelliği gösterdiği fakat *C. sinuosa*'dan elde edilen sodyum alginatın ise böyle olmadığı görüldü. Kahverengi alglerden elde edilen bu sodyum alginatların görülen viskoziteleri üzerinde temperatür etkisinin düşük kayma gerilimlerinde yüksek kayma gerilimlerinden daha etkili olduğu sonucuna varıldı.

* Marmara Uni. Faculty of Pharmacy, Department of Biochemistry, Nişantaşı - Istanbul.

INTRODUCTION

Seaweeds are classified into four principal groups: *Chlorophyceae,* the green algae; *Phaeophyceae,* the brown algae; *Rhodophyceae,* the red algae; and *Cynophyceae,* the blue-green algae (1). The *Phacophyceae* and the *Rhodophyceae* are primarily salt-water plants. They are commercially important because of their polysaccharide content and because they are available in quantities sufficient to support a sizable industry. Agar and carrageenan are extracted from various types of the red algae, and algin is derived from the brown seaweeds. These polysaccharides are spesific to seaweeds and are not found in land plants (2). The brown seaweeds, all of which contain algin, are an amazingly varied family of plants. The brown seaweed, which is the main source of algin, has properties which make it an ideal raw material for modern technology (3).

The first biochemical and pharmacological studies of Turkish marine algae were carried out by Kasım Cemal Güven et al (4) During the past twenty years Güven et al have estimated the amount of mannitol, alginic acid, agar, carrageenan, cellulose, bromocompound, alkaloid essential oils, sterols, free amino acids, protein and vitamin B_{12} in these algae (5). Özcan and Kadırgan (6) investigated the possibility of using Turkish marine algae as a source of dung. Seasonal and geographical variation in the alginic acid content of *Cystoseira barbata* was investigated by Atay (7).

Six species of Turkish brown seaweed were collected from Gökceada shores, the alginic acid content was estimated and sodium alginate was prepared from two of these species (*C. corniculata and C. sinuosa*). Their viscosity and mol weight were then estimated in this laboratory (8).

Sodium alginate is a very important raw material for many industries because its solution in water is very viscous. The viscous behaviour of sodium alginate when in water varies with species, season and location of seaweeds (9). The viscosity of sodium alginate solutions also varies with shear rate (rheology) (2, 10,11). The rheology of a solution of sodium alginate prepared from Turkish brown seaweed has not been investigated yet. The aim of the present work is to investigate the rheology, and the effect of the concentration and temperature on it, of the solutions of sodium alginate from *C. corniculata* and *C. sinuosa* collected from Gökceada shores.

MATERIAL AND METHODS

Preparation of sodium alginates from brown seaweeds: *C. corniculata* and *C. sinuosa* were collected from Gökceada shores in the Aegean Sea in June. The seaweeds were dried in the sun and subsequently pulverised with a hammer. The powder was washed in tap water, dilute HCl (0.5%, w/w) and distilled water and dried in an oven at 50°C. To dissolve the alginate the powder was stirred for 2 hrs at 70°C in 3% (w/v) Na_2CO_3 solution (100 ml/g. dried seaweed) and filtered. The filtrate was treated with dilute $CaCl_2$ to obtain Ca-alginate. The Ca-alginate gel was clarified with dilute NaOCl - solution and filtered through nylon mesh. In order to prepare alginic acid from this gel, Ca-alginate was treated with 5% (w/v) HCl solution (1:42, w/w) for 2 hrs, filtered and washed with distilled water. Alginic acid was titrated with dilute NaOH solution and gelatinized with ethanol. The sodium alginate gel was pressed and dried at 60°C, then redissolved with distilled water and centrifuged at 5000 rpm, for 30 min at room temperature. The clear supernatant was again gelatinized with ethanol and then dried. Two types of commercial sodium alginate were used for comparison: Protanal (Norway) and Kelco (U.S.A.).

The other chemicals were purchased from Merck (Germany). The date was obtained using Rheotest and a thermostat (Rheotest 2-50 Hz- Typ RV2, VEB MLW Prüfgeräte - Werk Medingen, Sitz Freital). Apparent viscosity can be calculated by applying different shear rates and using the following formula.

$$\text{Apparent viscosity (poises)} = \frac{\text{shear stress (dyn/cm}^2\text{)}}{\text{shear rate (1/sec)}}$$

RESULTS AND DISCUSSION

The comparison of the sodium alginate from *C. corniculata* and *C. sinuosa* with the sodium alginate from commercial sources (Protanal and Kelco, high viscosity sodium alginate) showed significant differences in apparent viscosity at all concentrations studied (Figure 1).

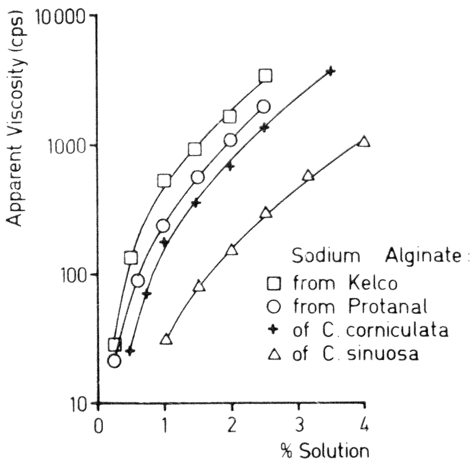

Figure 1: Viscosity/concentration curves for sodium alginate from C. corniculata, C. sinuosa and commercial sources at 20°C.

Sodium alginate from Turkish brown seaweeds has a low viscosity espacially that from *C. sinuosa*. The change in apparent viscosity of sodium alginate solution with shear rate indicates pseudoplastic behaviour. A 2% sodium alginate solution from *C. sinuosa* seems to be a Newtonian fluid. It was not possible to estimate the apparent viscosity of the solution below 81 sec^{-1} shear rate, because of the low reading of the indicator (Table I).

TABLE I

The change of apparent viscosity (cps) with shear rate for sodium alginate solution of C. corniculata and C. sinuosa at 20°C.

shear rate (sec^{-1})	sodium alginate of *C. corniculata* (%)			sodium alginate of *C. sinuosa* (%)		
	2	1	0.5	4	2	1
1.5	3318	592	—	2012	—	—
2.7	2734	461	—	1865	—	—
4.5	2470	433	—	1771	—	—
5.4	—	—	—	1576	—	—
8.1	1922	384	—	1418	—	—
13.5	1615	329	—	—	—	—
16.2	—	—	—	1383	—	—

24.3	1325	286	—	—	—	—
40.5	1054	249	—	1231	—	—
48.6	878	210	26	1127	—	—
72.9	832	207	25.9	—	—	—
81	812	184	25.8	1063	150.2	30.5
121.5	674	175	25.7	1007	148.5	29.7
145.8	586	158	25.6	939	142.1	29.4
218.7	511	146	25.5	869	140	29.3
243	460	135	25.4	829	131	28.4
364.5	398	120	25.3	742	123.7	28.2
437.4	355	107	24.5	690	119.7	27.3
656	293	91	22.1	—	114.2	26.4
729	275	87	22	—	110.5	26
1312	201	68	20.1	—	95.8	23.8

The pseudoplastic behaviour of sodium alginate solutions is related to the molecular weight of sodium alginate and the proportion of mannuronic and gluronic acid residues (9, 12). Sodium alginate of C. sinuosa, extracted with Na_2CO_3 solution has been shown to have a low molecular weight (about 1/3 of that of Kelco's high viscous sodium alginate (8). However the proportion of mannuronic and gluronic acid residues in sodium alginate from Turkish brown seaweeds is unknown, Unlike *C. sinuosa*, the sodium

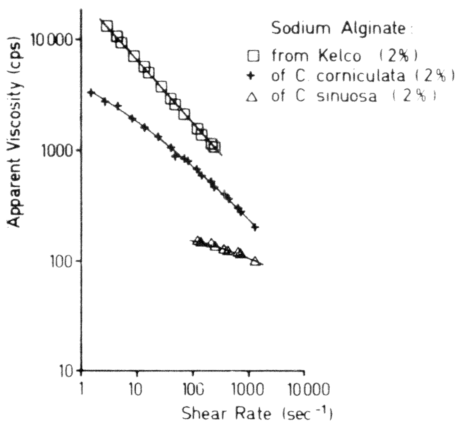

Figure 2: Apparent viscosity/shear rate curves for 2% solutions of sodium alginate from Kelco (high viscosity alginate), *C. corniculata* and *C. sinuosa*.

alginate from *C. corniculata* showed clear pseudoplastic flow behaviour by its relative steep flow curve, ist apparent viscosity at all possible shear rates was calculated (Fig. 2). The effect of the concentration of *C. corniculata* sodium alginate on the flow curve is shown in Fig. 3. At low shear rates the differences between the apparent viscosity of solutions of various concentrations are significant but become less at a shear rate greater than 100 sec^{-1}.

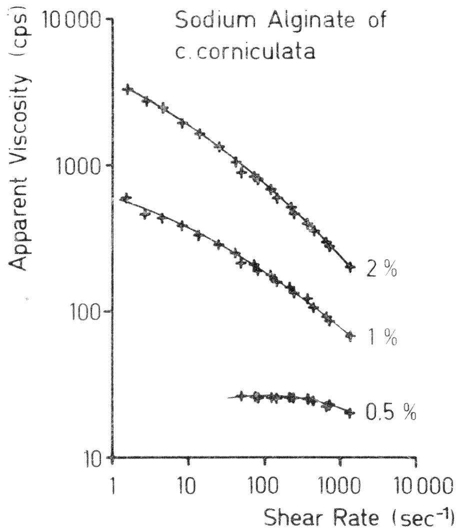

Figure 3: The apparent viscosity/shear rate curves for different concentrations of sodium alginate solution from *C. corniculata at* 20°C.

Fig. 4 shows apparent viscosity/shear rate curves for sodium alginate from *C. sinuosa* at 20°C. This sodium alginate shows a pseudoplastic flow behaviour at 4% concentration. At lower concentrations it behaves like a Newtonian fluid, as the difference between initial and final viscosities for each concentration is minimal. But for *C. corniculata* sodium alginate the differences between apparent viscosities of solutions of different concentrations remain significant at shear rates greater than 100 sec^{-1}. The effect of temperature on solutions of both sodium alginates is shown in Figs 5, 6. The change of apparent viscosity with temperature of sodium alginate solution from *C. sinuosa* is greater than that of *C. corniculata*. But the variability of both is not significant. The average change of apparent viscosity for every 10°C at low shear rates is more significant than at high shear rates (Table II). The temperature dependency of the apparent viscosity of sodium alginate from the two seaweeds was studied at different concentrations of sodium alginate because it was then easier to compare the viscosities.

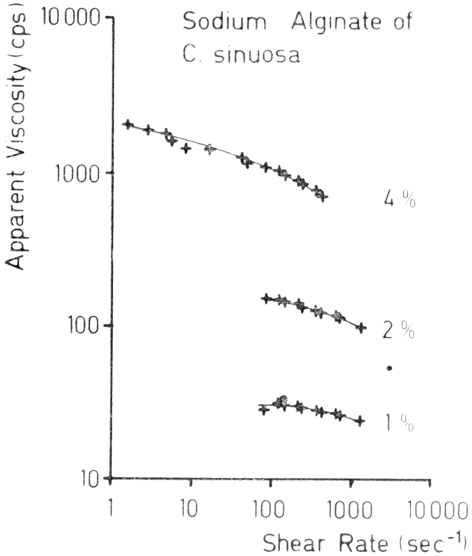

Figure 4: The apparent viscosity/ shear rate curves for different concentrations of sodium alginate solution from *C. sinuosa* at 20°C.

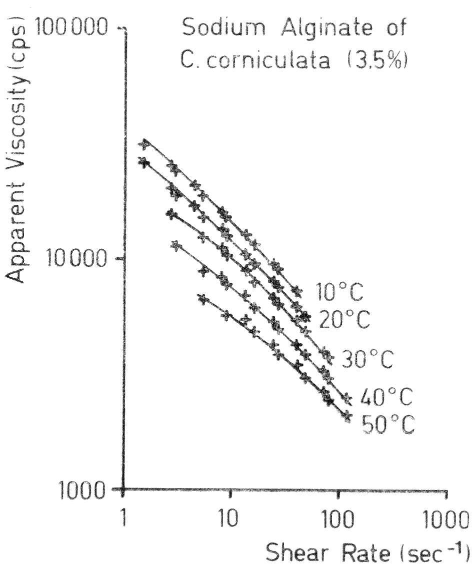

Figure 5: Apparent viscosity/shear rate curves for the sodium alginate solution from *C. corniculata* (3,5%) at 10-50°C.

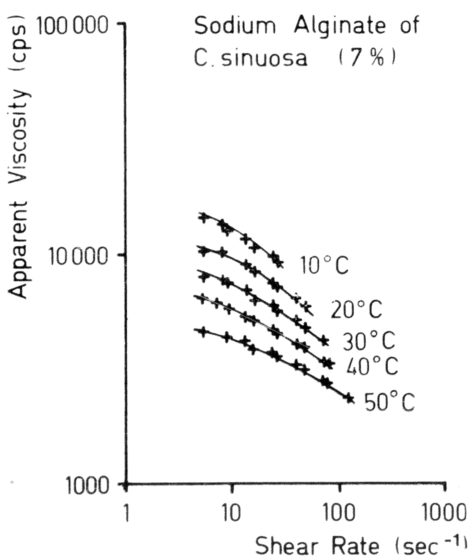

Figure 6: Apparent viscosity/shear rate curves for the sodium alginate solution from *C. sinuosa* (7%) at 10-50°C.

TABLE II. The changes of apparent viscosity (cps) of sodium alginates from *C. corniculata* and *C. sinuosa* with temperature.

	shear rate (sec^{-1})	10°C	20°C	30°C	40°C	50°C	a.v * / 10°C
C. corniculata sodium alginate (3.5%)	5.4	18652	15064	12340	8752	6596	22.7
	13.5	12628	10447	8840	6888	5395	18.9
	40.5	7270	6161	5357	4218	3443	16.8
C. sinuosa sodium alginate (7%)	5.4	14351	10184	7888	—	4558	24.5
	13.5	11481	8896	6888	5279	4131	22.5
	40.5	—	6314	5070	3980	3252	19.8

* The average change (%) of apparent viscosity per 10°C

REFERENCES

1. Chapman, V.J. : *Seaweeds and Their Uses.* 2 nd ed. Methuen and Co., London, 1970, p. 2.

2. Kelco : *Algin/Hydrophilic Derivatives of Alginic Acid for Scientific Water Control.* 2 nd ed. 1979, p. 3.

3. Maas, H. : *Alginsäure und Alginate,* 1959, p. 158-196.

4. Güven, K.C. and Aktin, E. : *Eczacılık Bülteni,* **12**, 199 (1962).

5. Güven, K.C. and Güvener, B. : *Chimica Acta Turcica,* 9, 389-394 (1981).

6. Özcan, E. and Kadırgan, N. : *Kimya ve Sanayi,* **24**, (108), 285 (1976).

7. Atay, D. : Doçentlik tezi, Ankara Üniv. Ziraat Fakültesi yayınları, Ankara 1974.

8. Peker, İ. : *Chimica Acta Turcica,* **12**, (3), 499-509 (1984).

9. Dowel, R.H. Mc. : *Soc. Chem. Ind. Monogr.,* **No. 24**, 19-32 (1966).

10. Mathieson, A.R. and Porter, M.R. : *Journal of Polymer Science,* **21**, 483-493 (1956).

11. Schutz, R.A. : *Die Stärke,* 22 (4), 116-125 (1970).

12. Haug, A., Myklestad, S., Larsen, B. and Smidsrod, O. : *Acta Chemica Scandinavica,* **21**, 768-778 (1967).

(Received October 14, 1985)