Binders for extrusion molding of ceramics.

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Abstract

Ceramic materials, unlike clay, are nonplastic when mixed with water and are thus impossible to form into any shape without the use of a binder. In extrusion molding of ceramics, methylcellulose is commonly used as a binder because of its unique properties of thermal gelation.

Water retention, lubrication, shape retention and crack prevention are important functions of a binder for extrusion molding of ceramics. The influence of ceramic/binder/water/etc. ratios in the extrusion molding mixture on the avove functions was examined.

1. Preface

Methylcellulose (MC) is a water-soluble linear cellulose ether polymer which has unique properties of thermal gelation when dissolved in water and heated, this polymer forms a gel which, on cooling, reverts to a liquid.

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The general process characteristic in extrusion molding of ceramics with a binder are summarized in Table1. The function of the binder may be simmarezed as follows.

(1) It should give sufficient water retention to prevent sepa-

ration of water as the pressure on the extrusion mixture is increased during extrusion molding.

(2) It should have a lubrication function (plasticity) to ensure smooth extrusion.

(3) It should ensure shape retention after molding.

(4) It should prevent crack occurrence owing to contraction distortion during drying after molding.

In the present work, the properties of methylcellulose as a binder for extrusion *molding* of ceramics were examined.

2. Thermal gelation of methylcellulose

Cellulose is linear polymer consist of D-glucopyranose units linked by β-(1→4) bonds, as shown in Fig.1. Because of the extensive interchain hydrogen bonding involving the hydroxyl-groups, cellulose does not dissolve in water. Methylcellulose is formed by substituting one or more of the three hydroxy groups of D-glucopyranose with metylgroups. This weakens the hydrogen bonding and increases the chain separation, so that hydration of the hydroxylgroups can occur and consequently the polymer can be dissolved.

Derevaties of cellulose substituted with various grups, such as methlyl, hydroxypropyl, etc. are used industry.

The number of substituted hydroxyl groups per glucopyranose residue is expressed as DS or average degree of substitution. The DS can vary between 0 and 3. In the case of hydroxyalkoxylation, the molar ratio of alkoxy groups in the side chains to cellulose is specified and expressed as the average molecular substitution (MS).

Methylcellulose dissolves in cold water, but not in hot water, probably because the hydration of the hydroxy groups mentioned above become less stable at higher tempereture. When a solution of methylcellulose is heated, it forms a white gel, which on cooling reverts to a solution. A theoretical analysis of this reversible thermal gelation was carried out by Takahashi et al(1). In methylcellilose, some of the D-glucopyranose residues will have all three hydroxul group methylated. When methylcellulose solution is heated, such trimethylated residues can form hydrophobic bonds as shown in Fig.2, resulting in thermogel formation.

These hydrophobic bonds become less stable again when the gel is cooled, and the solution is reformed. The relation between the thermal gelation temperature and methoxyl group and hydroxyalkyl group contents of methylcellulose derivatives is shown in Fig.3.

Methylcellulose (product name Metolose) for ceramic extrusion molding has been commercialized by Shin-Etsu Chem.Co.,ltd. Table-2 shows the grade of Metolose that are available. SM type has only methyl group substituted, while SH type has both methyl group and hydroxypropyl substitution.

The ash content of the binder eventually becomes impurities in the ceramic product, so a low ash content of the binder is desirable. Metolose can be purified by washing with hot water, since it does not dissolve in hot water. The standard ash content is not more than 1%, but ash can be reduced to below 0.5 % if necessary for special applications.

3. Water retention function of methylcellulose

The result of an evaluation of the water retention function of hydroxypropylmethylcellulose is shown in Fig.4.

Application of 16 t load to an extrusion mixtire resulted in release of some of the water content, and the amount released was measured. The amount decreased markedly as the binder volume was increased.

In comparison with methylcellulose, the water retention performance of polyvinylalcohol is inferior. When the amount of binder added is too small. water segregation occurs at the die of the extrusion molding machine. This may result in an excessive extrusion load. leading to breakdown of the extrusion molding machine. The extrusion mixture remaining in the extrusion molding machine then has a low water content.

4. Lubrication and shape retention

Effective lubrication means that the extrusion mixture can change its form easily in the molding machine during extrusion. Shape retention is required to maintain the form produced after extrusion.

Fig.5 shows the extrusion load observed when the extrusion mixture was forced through a 2 mm diamater cylindrical die using a 10 mm diamater piston, for various composition ratios of mixture. A low value of the load indicates good lubrication. Generally, a suitable pressure to allow smooth extrusion molding is about 50 kg/cm^2. when the amount of methylcellulose added is small, the pressure is high. As more methylcellulose is added, it is adsorbed on the ceramics surfaces and the pressure decreases to a minimum owing to the reduction of frictional resistance between the ceramic and the die wall. Further addition result in adhession to the die surface so that the pressure increases.

Softness is measured as the diamater of a 30 g ball of extrusion mixture at 2 minutes after placing a 2 kg weight on it. Small diameter indicates good shape retention. The relation between softness and extrusion mixture composition is shown in Fig.6. Too much binder and too little water result in a small softness value, so that the extrusion mixture becomes too hard. An extrusion load of about 50 kg/cm^2 as mentioned above,a softness value of 50 mm are suitable values for practical extrusion.

Fig.7 compares the effectiveness as binders of hydroxypropylcellulose (HPC), a water-soluble non-thermogelling and methylcellulose (MC). Methylcellulose gives superior shape retention at an equivalent level of lubrication. Fig.8 shows the extrusion load and softness values obtained with various water-soluble polymers at given extrusion mixture composition. Methylcellulose (MC) and hydroxypropyl methylcellulose (HPMC) seem to be the best binders under these conditions.

5. Crack prevention function during drying.

Binder (HPC and HEC) that lack thermal gelation ability and MC were used at a given extrusion mixture composition for thin sheet extrusion molding. The extent of cracking that developed in the sheet during drying was determind (Fig.9). As compared with sheets using HEC or HPC as a binder, the sheets using methylcellulose (MC) or hydroxypropyl methylcellulose (HPMC) binder exhibit greatly reduced crack occurrence.

6. Relation between thermogelling characteristic of MC and the binding function of MC in extrusion molding.

The concentration of methylcellulose relative to water is about 10 %-30 % in extrusion mixture. Therefore the gel strength of 10 % aqueous methylcellulose solution was measured. It decreased with increasing hydroxyalkyl MS, as shown in Fig.9. It is clear that gelation of the binder can greatly reduce or even eliminate crack occurence (see Fig.9). This is presumably because the gelation forms a three-dimensioal structure, which may inhibit crack formation. At 10 % or higher concentration of methylcellulose, it is possible that trimethylated residues in the polymer molecules may be able to form weak hydrophobic bonds to some degree, producing a three-dimensional gel-like structure, even at the extrusion temperature.

To examine the above possibility, the viscoelasticity of high binder concentration solutions at 20°C was compared for various kinds of binders having a number-average degree of polymerization of about 1000 (Fig.10). The finding that the dynamic-viscoelastic modulus of methylcellulose is particulary high in the high concentration area is consistent with the above idea that weak three-dimensioal structure is formed under these conditions. Thus, the thermogelling character of MC solution may be involved in shape retention and crack prevention.

Fig.11 shows a structure can also accunt for the effective water-retaining role of methylcellulose as a binder.

References

1) T. Kato, M. Yokoyama and A. Takahashi,"Melting temperature of thermal reversible gels," Colloid & Polymer Sci., 256, 15-21 (1978).

2) S. Nagura, S. Nakamura and Y. Onda,"Temperature-Viscosity relation of aqueous solution of cellulose ethers," Kobunshi-ronbunshu, 38, 133-137(1981).

3) Preprint of a new-ceramics adhesion technology lecture meeting on February 17, 1984. S. Nakamura "New ceramic extrusion molding using methylcellulose," p.1-8.

4) Polymer Society of Japan. Hokuriku Department. Preprint of 2nd binder symposium (1989) K. Hayakawa. "Binders for extrusion molding of ceramics,"p.29-35.

Table1. Process characteristics in extrusion molding of ceramics.

Process	Material blending.	Mixing (Kneading)	Extrusion	Drying (Cutting)	Sintering
Operation	Blending ceramic powder binder plasticiser water (several binders in aqueous solution)	· Dissolution Dispersing binder and ceramic pwder in kneader · Adjusting plasticity	· Extrusion under vacum	· Drying to keep extruded shape. · Cutting of dried component.	· Sintering · Burning out of binder
Nature or shape of material	Powder or granular	· Plastic component mixture	· Uniform phase	· Extruded component of adequate length	· Objective shape
Technical points	Uniform blending.	· Dissolving binder · Degradation of binder · Dispersing ceramic powder and binder solution	· Chill during exothermal extrusion · Maintain molding shape	· Prevent cracking during drying · Prevent distortion	· Prevent to cracking and distortion during sintering · Prevent contamination
Machine example	Henshell mixer	· Continuous kneader. · Three roll mill	· Screw vacuum extruder · Piston vacuum extruder	· Belt type dryer · Microwave dryer	· Electric furnace · Tunnel type furnace

Table2. Grades of Metolose (methylcellulose) available for use as binders in extrusion molding of ceramics.

Type		Methoxy groups		Hydroxypropyl groups		Viscosity (mpas)	Thermogeling temperature	Dissolution temperature
		wt. %	DS	wt. %	MS	(2%, 20°C)	(2%, 1°C/min)	
MC	SM	27.5- 31.5	1.8	-	-	15, 25, 100, 400, 1500, 400, 8000	-	20°C
HPMC	60SH	28-30	1.9	7-12	0.25	50, 4000	56°C	43°C
	65SH	27-30	1.8	4-7.5	0.15	50, 400, 1500, 4000	60°C	35°C
	90SH	19-24	1.4	4-12	0.20	100, 4000, 15000, 30000, 100000,	68°C	40°C

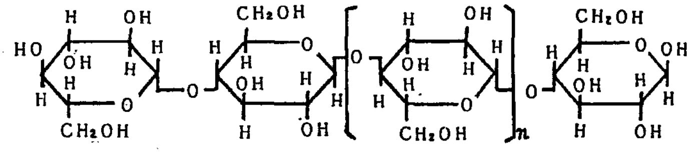


Fig. 1. Structure of cellulose.

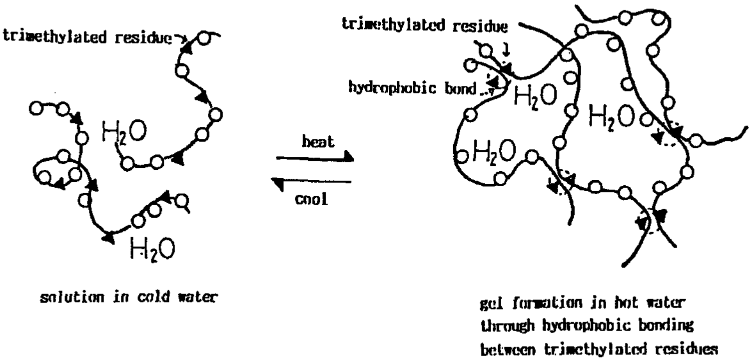


Fig. 2. Schematic illustration of the reversivible thermal gelation of methylcellulose.

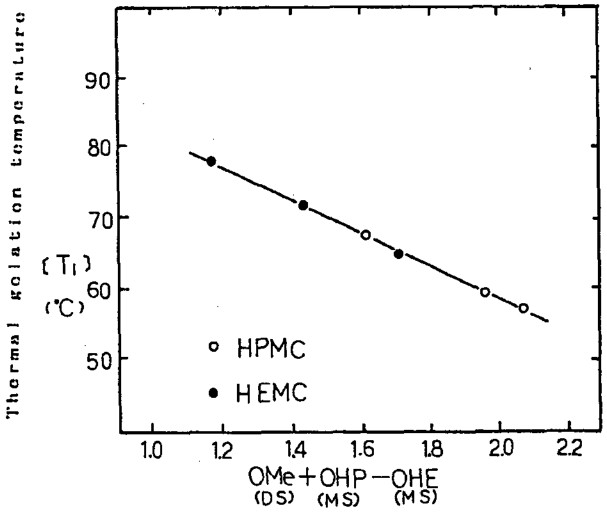
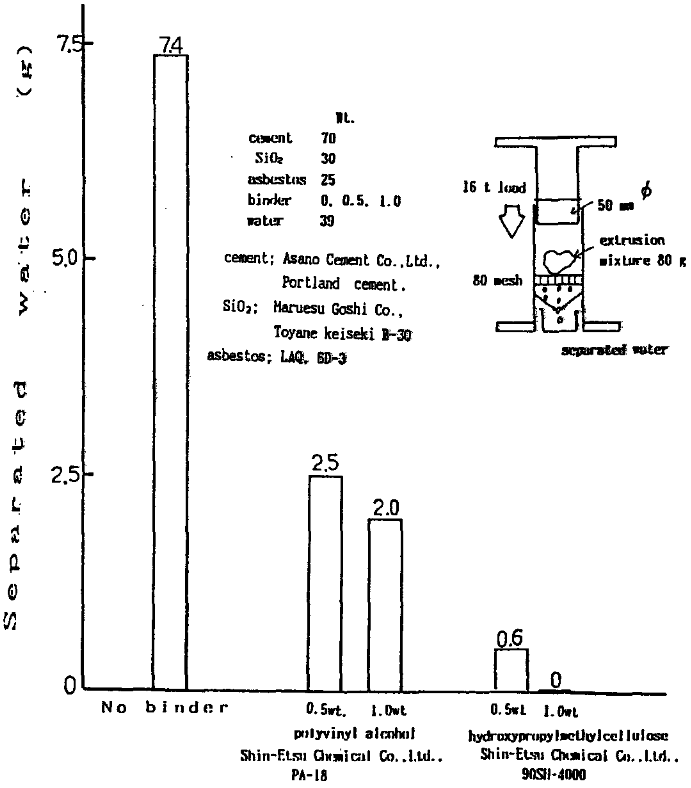


Fig. 3. Relation between thermal gelation temperature and substituent group content for hydroxypropyl methylcellulose and hydroxyethyl methylcellulose.



	Wt.
cement	70
SiO_2	30
asbestos	25
binder	0. 0.5. 1.0
water	39

cement; Asano Cement Co.,Ltd.,
Portland cement.
SiO_2; Maruesu Goshi Co.,
Toyane keiseki B-30
asbestos; LAQ, 6D-3

Fig. 4. Water retention function of hydroxypropyl methylcellulose.
The amount of water released from the extrusion mixture under 16 t load is shown.

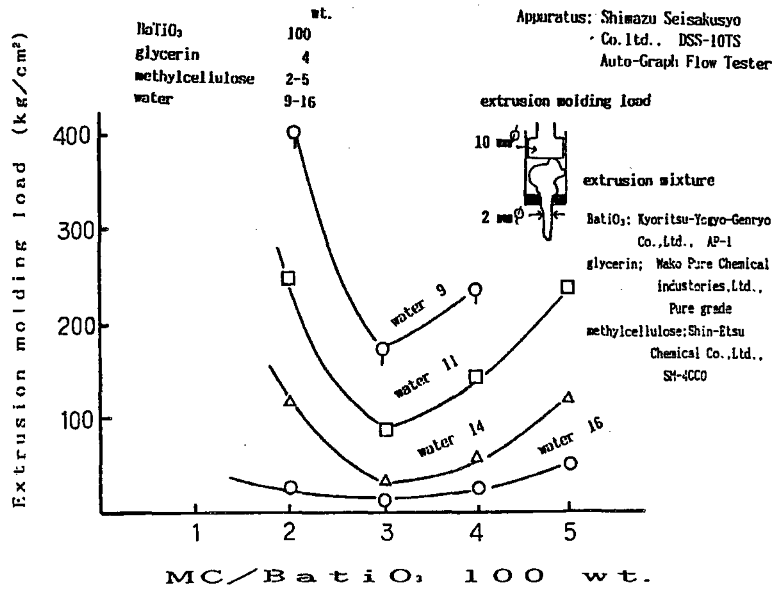


Fig. 5. Relationship of extrusion load to composition of extrusion mixture. A 10 mm diameter piston was used to force the extrusion mixture through a 2 mm diameter cylindrical die.

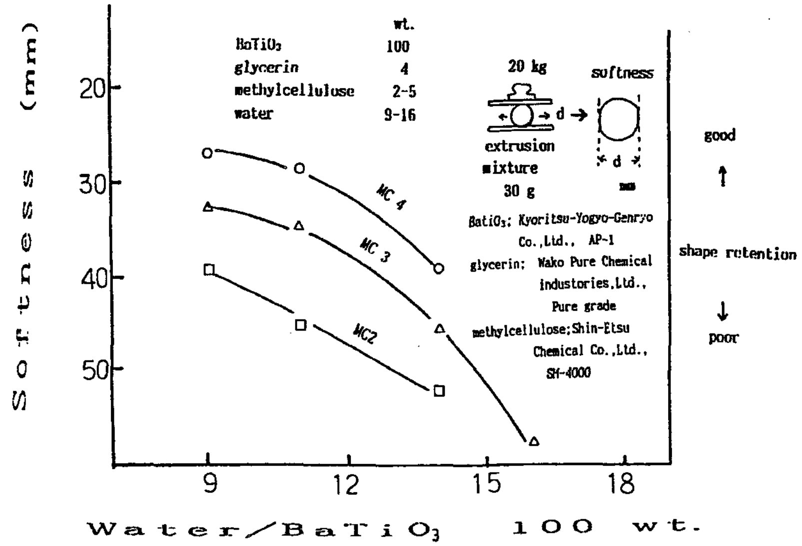


Fig. 6. Relationship of softness to composition of the extrusion mixture, reflecting shape retention after extrusion.

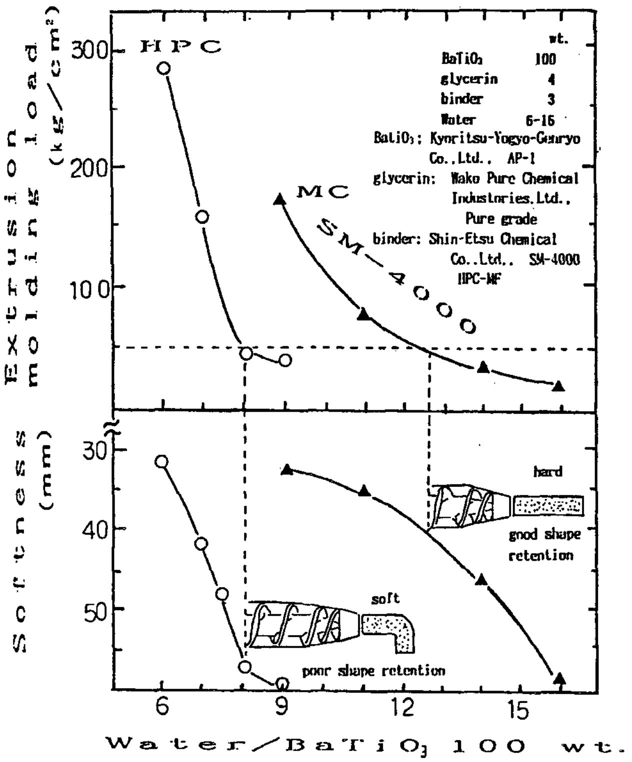


Fig. 7. Comparison of hydroxypropylcellulose and methylcellulose as binders for extrusion molding of ceramics in terms of softness of extrusion mixture and extrusion molding load.

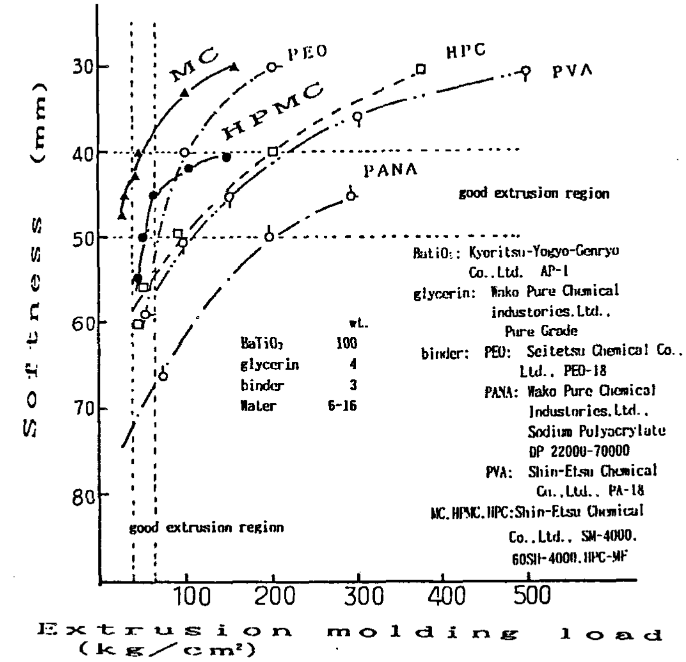
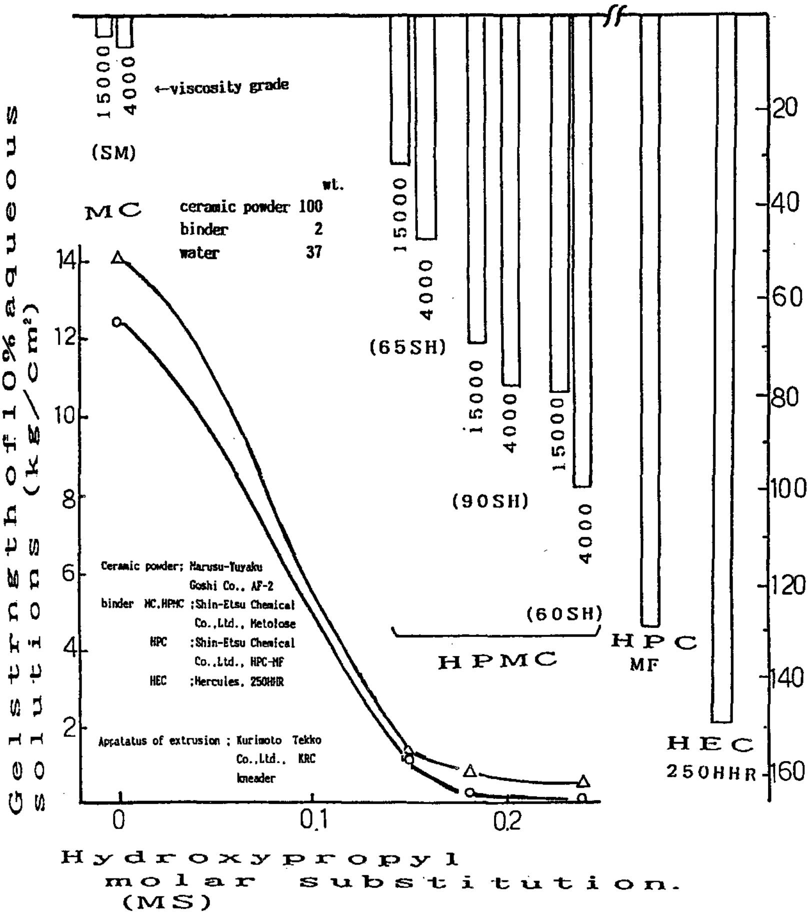


Fig. 8. Comparison of various polymer as binder at a given extrusion mixture composition.



	wt.
ceramic powder	100
binder	2
water	37

Ceramic powder; Marusu-Tuyaku Goshi Co., AF-2
binder MC,HPMC ;Shin-Etsu Chemical Co.,Ltd., Metolose
HPC ;Shin-Etsu Chemical Co.,Ltd., HPC-MF
HEC ;Hercules, 250HHR

Appatatus of extrusion ; Kurimoto Tekko Co.,Ltd., KRC kneader

Fig. 9. Degree of cracking that developed during drying of extrusion sheets formed with various polymers as binders.

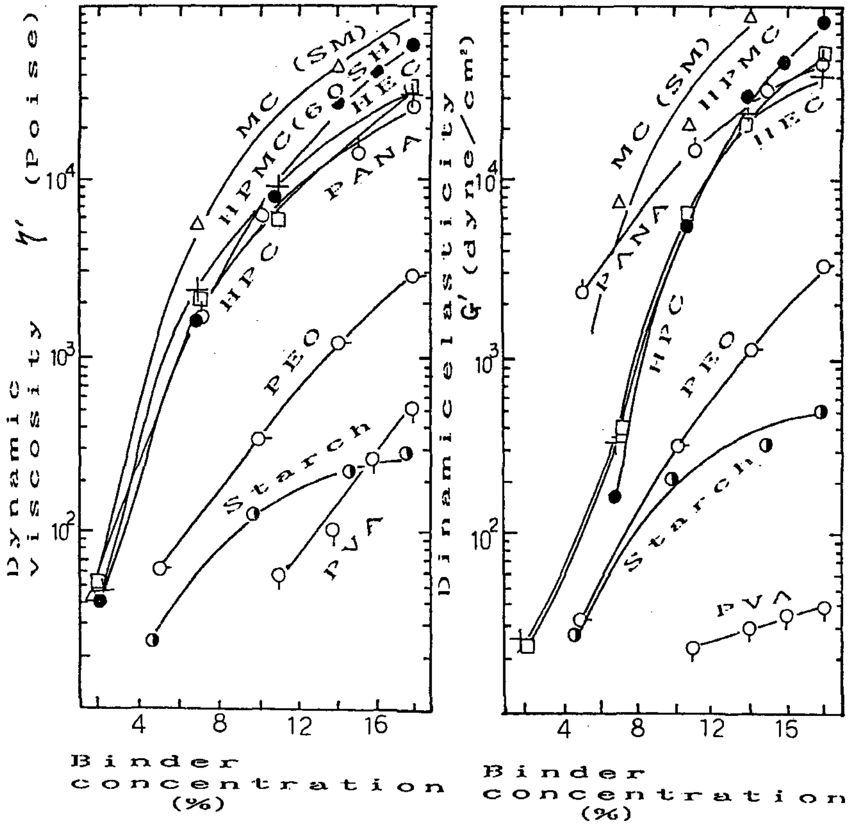


Fig. 10. Dynamic viscosity and dynamic elasticity of soluluons of various binders at high cncentrations.

MC;Methylcellolose. HPMC;Hydroxypropylmethylcellulose.
HEC;Hydroxy ethyl cellulose. HPC;Hydroxypropylcellulose.
PANA;Sodium polyacrylate. PEO;Polyethylen oxide.
Starch; α-starch. PVA;Polyvinyl alcohol

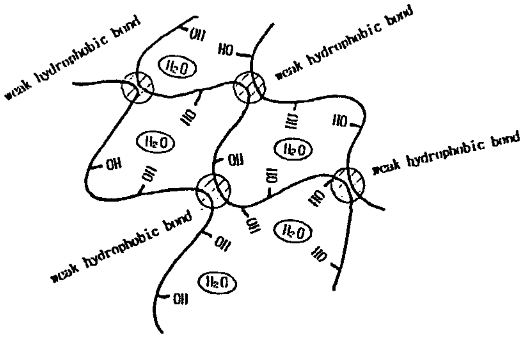


Fig. 11. Possible weak thre-dimensional structure of methylcellulose in solution of high cncentration.