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ANIONIC POLYELECTROLYTES CONTAINING MALEIC ACID UNITS AS SOIL CONDITIONERS

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A b s t r a c t. It was studied the effect of some anionic polyelectrolytes from maleic acid ammonium salt copolymers or terpolymers with vinyl acetate, methyl methacrylate or styrene on the structure of Cambic Chernozem soil Fundulea, Romania. This effect is determined by the chemical structure of the polyelectrolyte (the nature of comonomer(s)) and its concentration, the aggregate size being less important.

K e y w o r d s: polyelectrolytes, soil conditioners, Cambic Chernozem

INTRODUCTION

It is known that the structure of the soil is an important physical characteristic which determines its fertility. The soil structure influences directly or indirectly the other properties determining its air and water regime. It is dynamic and seasonal due to the climatological and agricultural conditions. An inadequate soil structure acts negatively on the germination and the emergence of the seeds and on the growth of the plants, mainly in the first vegetation phases. The state of soil structure is evaluated by means of some indexes: the water stability, the dispersion and the structure instability.

The treatment of soils with chemicals is a way to impart or preserve their structure. These chemicals include organic or inorganic substances with small molecules (gypsum, ferric sulphate, phosphoric acid or phosphates, lignosulphonates, quaternary ammonium salts, soap, higher aliphatic alcohols, etc.) or natural and synthetic polymers.

A review of polymeric soil conditioners is given by Azzam [1]; other polymers are cited by de Boodt [7]. A possible classification of the polymers used as soil conditioners is:

- water insoluble polymers (as suspensions, emulsions, latexes): polydienes and natural rubber, poly(meth)acrylates, polystyrene and styrene copolymers, poly(vinyl acetate) and vinyl acetate copolymers; polyurethanes, ureaformaldehyde resins, polysiloxanes;
- water soluble polymers: polyacrylamides, poly(ethylene glycol)s, poly(vinyl alcohol) and its derivatives, poly(N-vinylpyrrolidone);
- polyelectrolytes (linear polymers having positively and/or negatively charged groups): poly(acrylic acid) and its salts, hydrolysed poly(acrylonitrile), copolymers of maleic anhydride /acid with vinyl acetate or isobutylene, polymers and copolymers of 2-acrylamido-2-methylpropane sulphonic acid, sodium or potassium salt of poly(styrene sulphonic acid), quaternised polyvinylpyridine.

After an upsurge of R + D effort concerning the soil treatment with polymers in the 50s and after a period of stagnation now a come-back is obvious. In the context of the world food crisis, the polymers have become competitive although they have a relatively high price [5,8].

The use of some anionic carboxylic polyelectrolytes, as soil conditioners is already known, for instance maleic acid copolymers, ammonium or sodium polyacrylate, hydrolyzed polyacrylamide, hydrolyzed polyacrylonitrile [11,13]. Systematical attempts use some carboxylic polyelectrolytes from maleic acid copolymers (Ponilit GT^{R*} and Ponilit A-1^{R*}) for treating the Romanian soils have been made in laboratory and in field for several years in various soil and climate conditions with favourable results [2,6,12].

In this paper we intend to present some of our observations on the influence of the nature of the comonomer associated with the maleic acid in some anionic polyelectrolytes on the physical characteristics of the soil forming the seedbed of the fields cultivated with seeds sensitive to the build-up of crusts (sugar beet).

EXPERIMENT

Polyelectrolytes

Three copolymers and three terpolymers of maleic anhydride with vinyl acetate, methyl methacrylate or styrene were synthesized by our own methods [3]. The chemical composition of the copolymers was determined according to a known method [4] by conductometric titration in acetone: water mixture (1:1 vol) with aqueous N 0.1 sodium hydroxyde, using a Radiometer A.B. Copenhagen conductivity meter type CDM 2d and a conductivity cell CDC 114. For the terpolymers, after the conductometric titration of the maleic acid units, the content of methyl methacrylate, vinyl acetate and styrene units was estimated from H-NMR spectra, using the peaks at 3.75; 5.5; and 7.4 mg/kg, respectively. The spectra were recorded with a JEOL NMJ 60 MHz spectrometer, using deuterated acetone as solvent and its signal at $\delta = 2.05$ mg/kg as internal standard. The corresponding polyelectrolytes were obtained from these maleic anhydride copolymers by hydrolysis with water of the anhydride ring and neutralisation with ammonium hydroxyde 25 %. The synthesis conditions and the characterisation of the synthesized products are presented in Table 1.

Soil

The trials were made on laboratory model samples using a soil drawn from the superficial seedbed of Cambic Chernozem from Fundulea (Calarasi, Romania). Its characteristics are: clay content 34 % (particles smaller than 0.002 mm in diameter) corresponding to a clayey loamy texture, about 3 % organic matter (humus) and pH = 6.4. The soil taken from the field was separated by dry sieving into the following fractions: 0.25-1.0, 1.0-2.0, 2.50-4.0 and 4.0-6.3 mm. For testing aqueous solutions were prepared with 0.1, 0.3, 0.5, 0.7 and 0.9 % polyelectrolyte contents. A soil treated with the same amount of water was used as control sample. The amount of polyelectrolyte solution necessary to moisture the soil samples to obtain a water content corresponding to the field capacity was calculated taking into account the present moisture content which was about 10 %, a level corresponding to the wilting point.

To follow up the effect of the polyelectrolytes on the structure of the soil samples we made analyses and determinations of : a) water stability of the aggregates larger than 0.25 mm in diameter; b) dispersion (small particles with a diameter between 0.01 and 0.02 mm) and c) structure instability (an index calculated according to the Henin's method, modified by the Institute for Soil Science and Agrochemistry (ICPA) Bucharest [9,10].

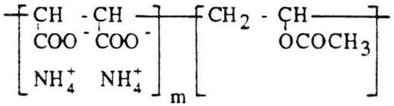
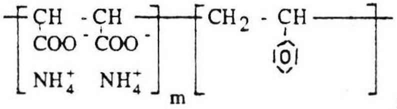
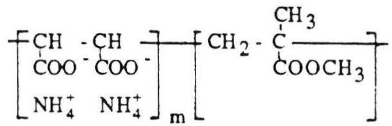
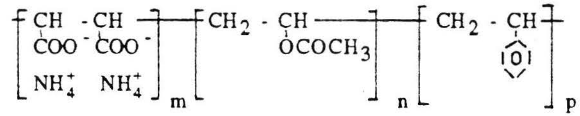
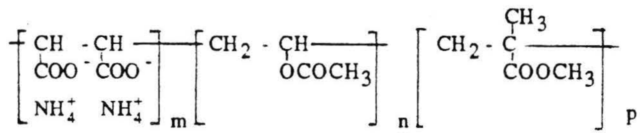
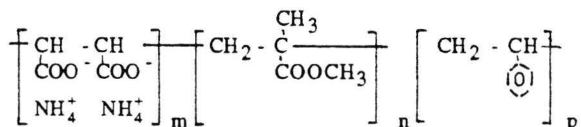
RESULTS AND DISCUSSION

The characteristics of the soil treated with the six polyelectrolytes are shown in Figs 1-3.

The data concerning the water stability

* Ponilit GT and Ponilit A are registered trade marks of 'Petru Poni' Institute of Macromolecular Chemistry, certificate 12297 February 1986, granted by OSIM Romanian State Invention and Mark Office.

Table 1. Synthesis and characterisation of the maleic anhydride copolymers and terpolymers with vinyl acetate, methyl methacrylate and styrene

Sample	Synthesis and purification conditions for copolymers and terpolymers					Chemical structure of corresponding polyelectrolyte determined by conductometric titration and from H-NMR spectra	
	Copolymerization technique	Solvent	Precipitation and filtration	Dry spraying	Extraction with benzene 24 h		
Ponilit GT-1	solution-suspension	benzene	yes	no	yes		m : n = 1 : 1
AS 1.1	solution-suspension	toluene	yes	no	yes		m : n = 1 : 1
AM 46.1	solution	MEC*	yes	yes	no		m : n = 1 : 1.33
ATS 27.1	solution suspension	benzene	yes	no	yes		m:n:p= 1:0.54:0.46
ATM 10.1	solution	MEC	no	yes	yes		m:n:p= 1:0.53:0.43
ATMS 2.1	solution	MEC	no	yes	yes		m:n:p= 1:0.32:0.68

* MEC - 2 - butanone.

correlated with the chemical structure of the polymer and its concentration (Fig. 1) indicate that nearly all values are considered as 'very high' and 'extremely high' (over 60 %). The best results were obtained with the polyelectrolytes AS 1.1 and ATS 27.1 which provided extremely high values of the water stability (63-77 %) without respect of the concentration, the value for untreated soil being 2 %. Both polyelectrolytes have hydrophobical styrene units and produce an increase of the water stability at low concentrations (0.1-0.3 %), unlike the polyelectrolytes containing vinyl acetate units (Ponilit GT-1, ATM 10.1) which cause a gradual increase of water stability with respect to their concentration, the maximal value being only reached at c=0.9 %.

The results obtained for the dispersion (Fig. 2) show a decrease of the small particle content to 2.5 % with ATS 27.1 (c=0.5 %), to 2.6 with AM 46.1 (c=0.7 %), unlike the value of 7 % obtained with ATM 10.1 (c=0.1 %). For comparison, the dispersion of the treated soil is 10 %. The best values for the dispersion were obtained using either polyelectrolytes with fewer styrene units (ATS 27.1) or polyelectrolytes containing only methyl methacrylate as comonomer (AM 46.1).

The structure instability of the treated soil (Fig. 3) has values considered as very low (0.03-0.13) beside 2.67-11.00 for the untreated soil. One can notice that the lowest values were obtained with the polyelectrolytes ATS 27.1 at concentrations of 0.3-0.5 %, with ATMS 2.1 at 0.7 % and with AS 1.1 at 0.1 %.

Once again one can notice the favourable effect due to the presence of the hydrophobical styrene units in the macromolecular chain, but at a concentration lower than the one of the binary copolymer AS 1.1 and associated with monomer units of vinyl acetate or methyl methacrylate.

These observations may be used to understand better the mode of action of polyelectrolytes on the soil particles/components. It is mentioned the polyelectrolytes improve the properties of soil as an effect of two different actions: their adsorbability on the soil particles and their flocculating capacity [1]. These two effects appear to us be partially overlapping. De Boodt [8] resumes the findings concerning the mechanism of interaction between the synthetic polymers and the soil particles or the soil units as follows: the charged polymers (i.e., polyelectrolytes) act by direct coulombian interaction or by bridging through of polyvalent inorganic ions, while the binding of uncharged polymers might be somehow more complex. Our results would suggest that the influence of the polyelectrolyte on the soil stucture is produced not only by ion-exchange between polyelectrolyte and soil particle, due to the maleic units which are present in all studied polymers, but also by physico-chemical interactions (Van der Waals, hydrophobic forces) depending on the chemical structure of the comonomer/comonomers. The comonomer can modify the global effect of the polyelectrolyte: the styrene units can make the soil hydrophobic (we have really noticed this effect) imparting its water stability. Vinyl acetate and methyl methacrylate are adhesive and improve the dispersion by weak binding forces.

Concerning the effect of the polyelectrolytes on the different size classes of the soil aggregates, the best results are obtained for the medium size fractions (between 2.5 and 4.0 mm) but the differences are small enough (Table 2).

However, the data presented before are preliminary, making evident the complexity of the polyelectrolyte soil particle interactions and justifying further studies concerning the adsorption of these polyelectrolytes on the soil particles, their elution from the particles, the ion-exchange between polyelectrolyte and soil particles, the influence of the molecular weight and the counterion of the polyelectrolyte, the morphological aspects of the treated soil, etc.

CONCLUSIONS

The polyelectrolytes containing maleic acid units have a favourable influence on some structural indexes of the Rumanian Cambic Chernozem samples. The best results were

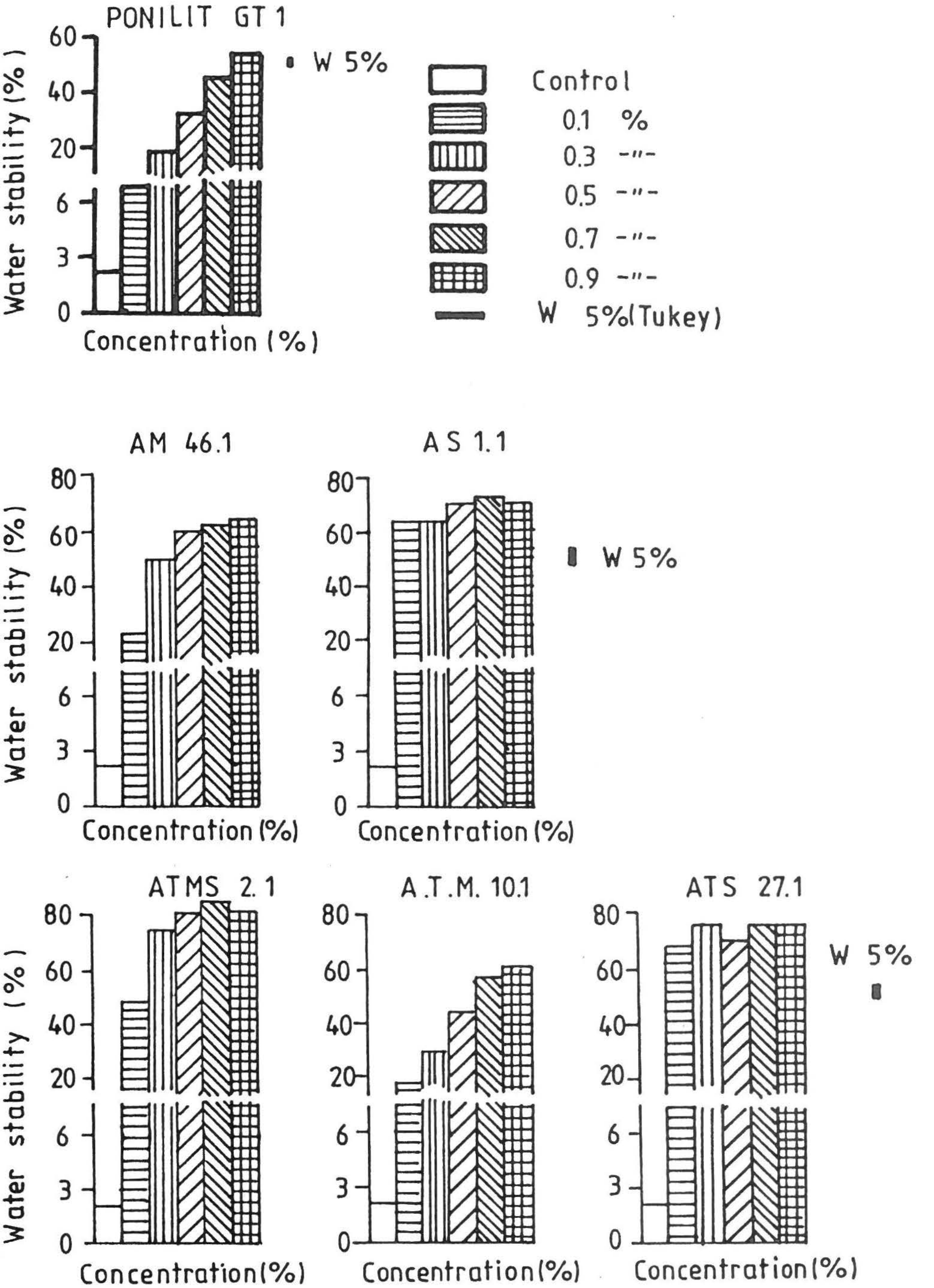


Fig. 1. Water stability of soil aggregates > 0.25 mm in diameter treated with different concentrations of various polyelectrolytes. For description of chemical structure of polyelectrolytes treated - see Table 1.

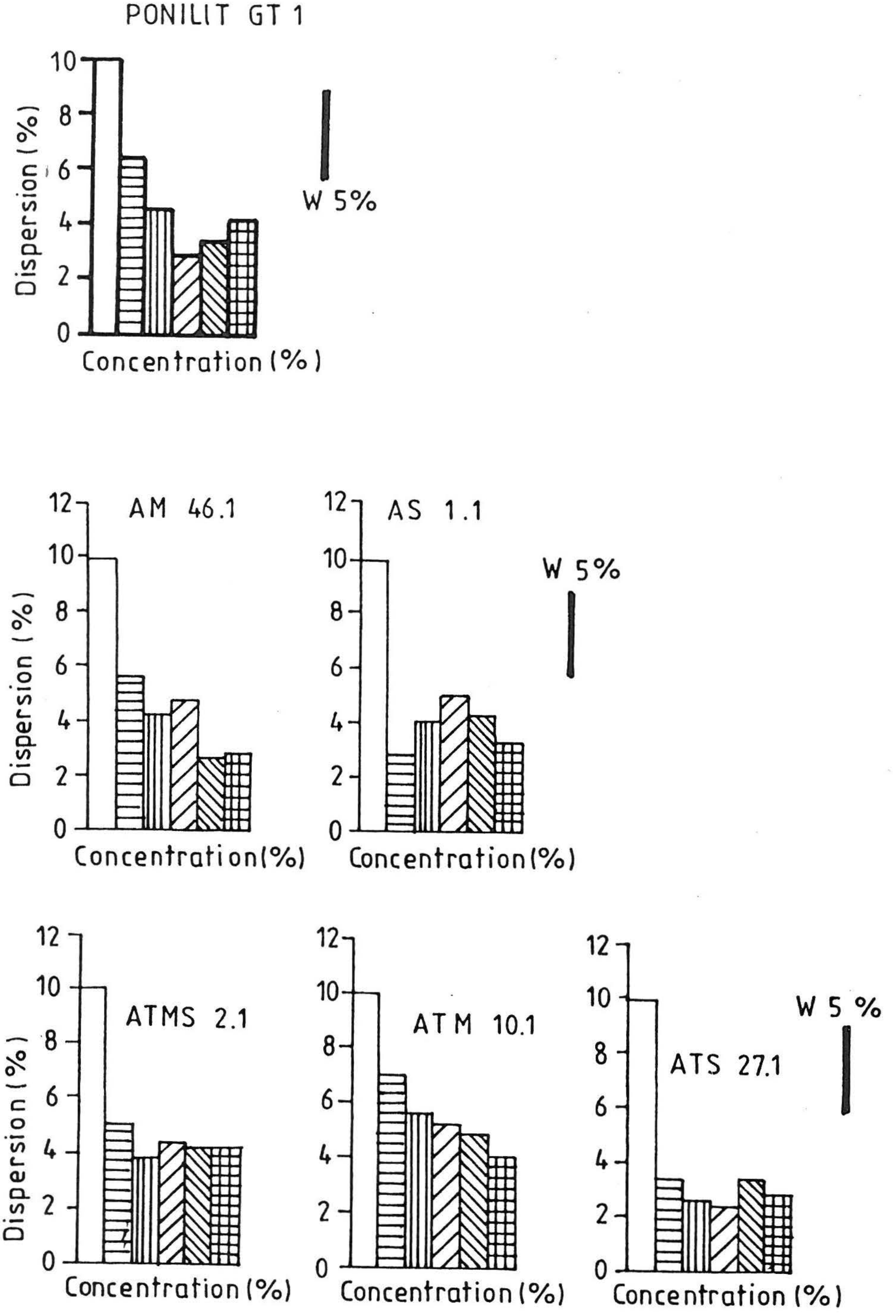


Fig. 2. Dispersion of soil samples (% content of particles 0.01-0.02 mm) treated with various polyelectrolytes.

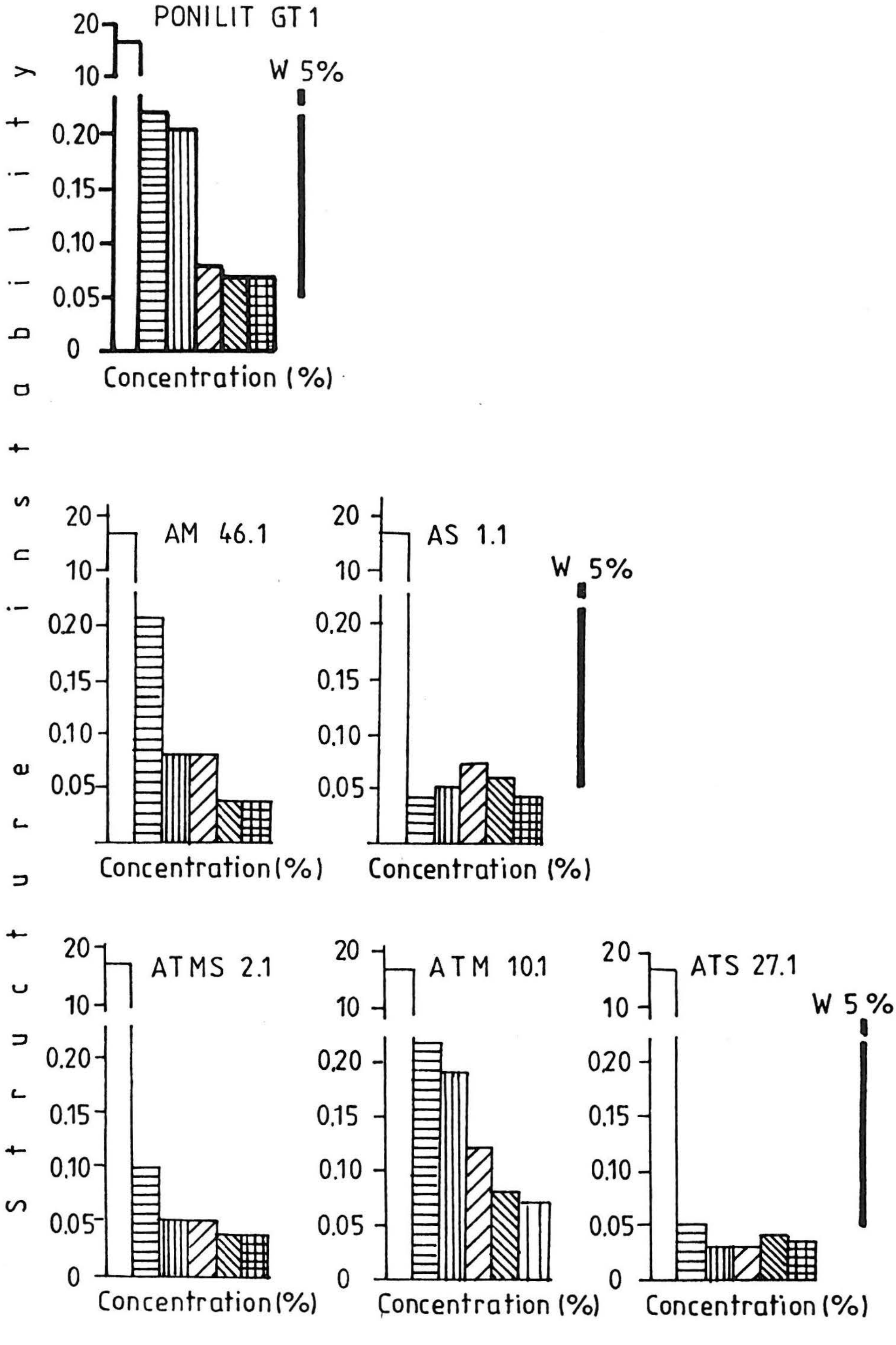


Fig. 3. Structure instability index of soil samples treated with various polyelectrolytes.

Table 2. The effect of the polyelectrolytes on the structure of Chernozem of Fundulea, Romania for the different particle sizes

Aggregate size (mm)	Concentration of polyelectrolyte solution (%)	Water stability (%)	Dispersion (%)	Structure instability
	0	2	11.9	59.5
	0.1	29	7.3	0.89
0.25 - 1.00	0.3	49	4.0	0.10
	0.5	54	4.1	0.08
	0.7	61	3.2	0.06
	0.9	63	4.4	0.07
	0	3	9.3	3.10
	0.1	33	5.7	0.49
1.00 - 2.00	0.3	52	4.8	0.13
	0.5	59	4.6	0.98
	0.7	64	3.9	0.06
	0.9	65	3.0	0.04
	0	3	8.0	2.67
	0.1	37	2.8	0.23
2.50 - 4.00	0.3	55	4.1	0.09
	0.5	62	4.4	0.07
	0.7	66	4.7	0.07
	0.9	68	4.5	0.07
	0	1	11.0	11.00
	0.1	38	5.3	0.31
4.00 - 6.30	0.3	54	4.5	0.10
	0.5	62	4.9	0.08
	0.7	67	5.4	0.09
	0.9	66	4.2	0.07

obtained with polyelectrolytes which are terpolymers of maleic acid ammonium salt having in the macromolecular chain styrene comonomer units 'diluted' with vinyl acetate or methyl methacrylate units.

The effect of the polyelectrolyte is dependent on its concentration, but the results obtained at lower concentrations are acceptable, so that they can become economically efficient.

The influence of the polyelectrolyte is less dependent on aggregate size, the best results being obtained for the medium size fractions.

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REFERENCES

1. **Azzam R.A.I.:** Agricultural polymers. Polyacrylamide preparation, application and prospects in soil conditioning. Commun. Soil Sci. Plant Analysis, 11, 8, 767-834, 1980.
2. **Canarache A.:** The Physics of Agricultural Soils (in Rumanian). Ceres, Bucuresti, 1990.
3. **Carpov A., Chitanu G., Maftei M., Zamfir A.:** Process of synthesis of carboxylic polyelectrolytes (in Rumanian). Pat. 70 120, 1979.
4. **Caze C., Loucheux C.J.:** Mechanism of alternating copolymerization of vinyl acetate and maleic anhydride. J. Macromol. Sci. Chem., A9, 29-44, 1976.
5. **Chamberlain P.:** Chemistry in Britain. 144-6, 1988.
6. **Chivulete S., Carpov A., Chitanu G., Maxim S.:** Process of soil structure stabilization (in Rumanian). Pat. 102205, 1991.
7. **De Boodt M.F.:** Applications of polymeric substances as physical soil conditioners. In: Soil Colloids and Their Associations in Aggregates. (Ed. M.F. de Boodt et al.). Plenum Press, New York, 517-556, 1990.

8. **De Boodt M.F.**: Synthetic polymers as soil conditioners: 35 years of experimentations. In: Water Saving Techniques for Plant Growth. (Ed. H.J.W. Verplancke et al.). Kluwer Academic Publishers, Netherlands, 137-161, 1992.
9. **Dumitru E., Trandafirescu T., Chivulete S., Olingheru M.**: Works rules for the determination of the characteristics of soil structure. Methods elaborated by the Research Institute for Soil Science and Agrochemistry, Bucharest, 1987.
10. **Henin S.**: Cours de Physique du Sol. Orstom Editest, Paris-Bruxelles, I, 1976.
11. **Metalova S.N., Shpilevskaya I.N., Akhmedov K.S.**: Effect of PAN saponification time on the properties of the structure-forming Agent K-7. Dokl. Akad. Nauk Uzb. SSR, 27, 4, 1-40, 1970.
12. **Pascu A., Angelescu M., Badiu A.F.**: Cerinte agrotehnice pentru realizarea unor productii ridicate de sfecla de zahar in anul 1988. Rev. Productia Vegetala, Cereale si plante tehnice, Rumania, 3, 31-35, 1988.
13. U.S. Pat. 2.891.931, 23.06. 1959; Austr. Pat. 202. 579, 10.03. 1959; U.S. Pat. 3.033.782, 08.05.1962; U.S.Pat. 3.312.070, 04.04.1967.