RHEOLOGICAL APPROACH FOR AGRICULTURAL HYDROGELS

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Abstract

A soil in region of Czech Republic and Austria is continuously losing its natural property to retain water in its structure. Most of the water which comes from rains just goes through the soil into the groundwater and agricultural lands suffer by the lack of humidity. One of the reasons of this strange soil behaviour is caused by decreasing amount of organic soil matter. Solution of this problem can be found in application of superabsorbent polymers enriched by addition of active substance based on humic acids. This system of controlled released preparation is able to retain more water in the ground together with sustainable supply of humic acids which are important part of organic soil matter. Rheological properties of samples superabsorbent polymers enriched by humic acids were determined to prove if they are able to resist certain mechanical mechanical stress which they will have to hold out after agricultural application.

Keywords: Superabsorbent, Hydrogel, Controlled release, Fertilizer, Rheometry, Swelling

1. INTRODUCTION

Many researchers are trying to solve the problem with continuous increasing degradation of agricultural lands. The ground is still more and more devastated mainly because of its wasteful cultivation and excessive fertilization. These facts have big impact on the loss of soil organic matter. The solution of these problems can be found in application of humic substances which constitute the most ubiquitous source of soil organic matter in nature [1]. They have important role in soil fertility such as stimulating plant growth, enhancing the resistance of crops, improving soil structure and increasing soil retention of water and fertilizer [2].

The most important fraction of humic substances are humic acids [3]. There is a very compex way of their dissolution in the water solution which affects their transport from soil into the herbal body [4]. Research of humic acid's transportation is very important mainly because of our understanding of their function in nature [4 – 7]. They are able to difusse themselves through various environment moreover they can work as a transport vehicle for other compounds [7]. The application of humic acids into the environment is very important especially for their ability to form water-soluble complex in reaction with metals [8 – 11].

Superabsorbent polymers are loosely crosslinked, three dimensional networks of flexible polymer chains that carry dissociated, ionic groups which cause their ability to absorb large quantities of water and other aqueous solutions without dissolving by solvation of water molecules via hydrogel bonds.

Superabsorbent polymers have a wide range of usage. In the field of agriculture and environmental protection they are very often used as a water hanger during a dry season nowadays. In contrary they avoid to decay of plants' root system in the time of heavy rains. There is a new trend in a field of superabsorbent polymers and it is an incorporation of fertilizers into the gel structure. This can be consider as a functional system which allows controlled release of substances that support growing and maturing of plants. Such mechanism solves the problem with flushing of fertilizers into deep underground water and avoids to overferilize of ground as well [12].

In this work, novel superabsorbent material for agricultural and environmental application was reported. The properties of specific superabsorbent polymers are extremely important for selecting a material for a given application. Here will be discussed method of characterizing superabsorbent polymers using rheological techniques to probe their mechanical response. Further, there will be comparison of their swelling behaviour.

1. EXPERIMENTAL

1.1. Materials

Six different samples of superabsorbent polymers based on acrylic acid were used in this work. All of them have a certain addition of NPK fertilizer. Some of them have also an addition of humic substance in a form of commercial lignohumate. Furthermore the samples also differ in a content of acrylamide in the structure. There was big effort to avoid presence of acrylamide in the structure of superabsorbent because of its toxicity. Accurate representation of these selected substances can be found in Table 1.

Table 1 Composition of superabsorbent samples

sample	A	B	C	D	E	F
NPK [%]	1	10	1	10	1	10
lignohumate	no	no	yes	yes	Yes	yes
acrylamide	yes	yes	no	no	Yes	yes

These samples were prepared in cooperation with Amagro, s.r.o. company and their composition will not be specified in more details because of the intellectual property protection.

1.2. Swelling measurements

Monitoring of swelling behavior was carried out by very simple method, sometimes referred to as “tea bag” method. 0.5 g of each sample was immersed in excess distilled water of volume 200 mL at room temperature for 24 hours to reach the swelling equilibrium. Swollen samples were then separated from unabsorbed water. Water absorbency in distilled water of the superabsorbent composite Q, was calculated using the following equation:

$$Q = \frac{m - m_0}{m_0}, [\mathrm{g/g}] \tag{1}$$

where m_0 and m are the weights of the dry sample and swollen sample, respectively. Q is calculated as grams of water per gram of dry sample. On the Figure 1 a) is displayed xerogel of superabsorbent polymer before immersion to the excess of distilled water. On the b) there is a swollen gel after 24 hours in the water.

Figure 1 a) Xerogel of superabsorbent polymer. b) Swollen suberabsorbent polymer.

1.3. Viscoelastic measurements

The viscoelastic experiments of the fully swollen superabsorbent polymer particles were carried out in Anton Paar Physica MCR 501 rheometer (see Figure 2) partially according to a previously reported method [14]. The measurement was done at 30 ± 2 °C using a parallel plate system (PP25-SN6375, 1 mm diameter) at 1 mm gap. Viscoelastic measurements, oscillation – frequency sweep and strain sweep, were performed for each sample and the obtained values of moduli G´and G´´ were compared. Storage modulus G´ is proportional to the extent of the elastic component and loss modulus G´´ is rational to the extent of the viscous component of the system. The strength of materials is measured by the magnitude of tan δ (the ratio G´´/G´), where δ is a phase angle.

Figure 2 Anton Paar Physica MCR 501

2. RESULT AND DISCUSSION

Swelling behaviour of all superabsorbent samples were determined by the measurement of water absorbency. The results show that all samples exhibit very good swelling properties, as it is displayed on

Figure 3. The results revealed some interesting findings. The samples differed from each other by special composition that is shown in Table 1. There is a significant negative effect on superabsorbent swelling properties caused by the higher content of NPK in the structure of sample. These samples B, D and F reflect much lower ability to absorb surrounding water and they were not followed to the further testing. Samples with an addition of lignohumate swelled significantly better than samples without lignohumate. That is caused by hydrophilic character of lignohumate.

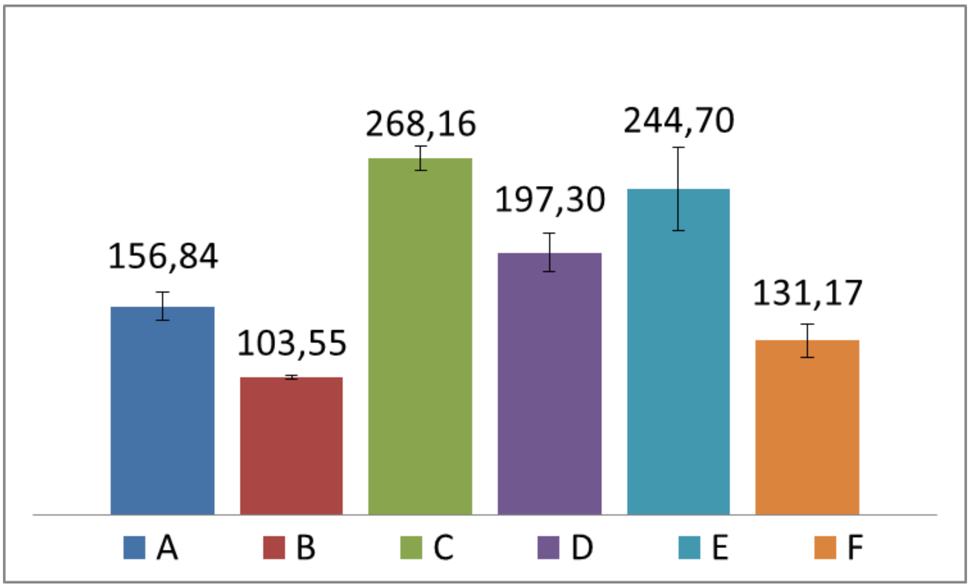

Figure 3 Water absorbency Q of SAP samples, [g/g]

Viscoelastic studies of these swollen superabsorbent samples were determined by means of the rheological method. Determination of the linear viscoelatic region was performed by strain sweep experiments. Loss modulus and storage modulus are independent of the stress amplitude as it is displayed on Figure 4. The storage modulus was always larger than the loss modulus at the linear viscoelastic region.

Values of tan δ are plotted in Figure 5. As is mentioned before, tan δ is the ratio of G´´/G´, where is a phase angle. If the value of tan δ is larger than 1, it means G´´ is higher than G´, the system behaves like a liquid. In contrary, if the value of tan δ is smaller than 1, it means G´´ is smaller than G´, the superabsorbent exhibits solid-like behaviour. Accordingly, the strength of the interaction or network structure is basically measured by the magnitude of tan δ. The smaller the tan δ is, the stronger the interaction becomes. There are results which show that the strength of the superabsorbents inversely correlates with their water absorbency.

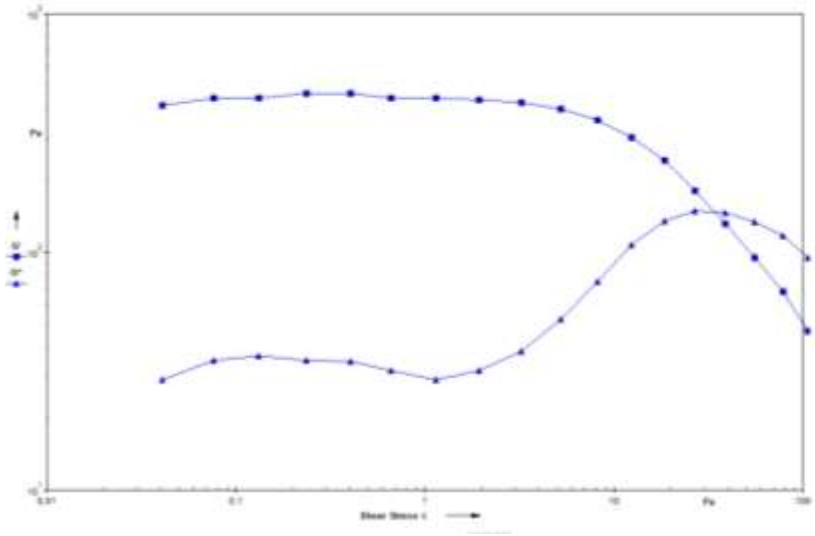

Figure 4 Example of measured viscoelastic properties of the supeabsrbent **.**

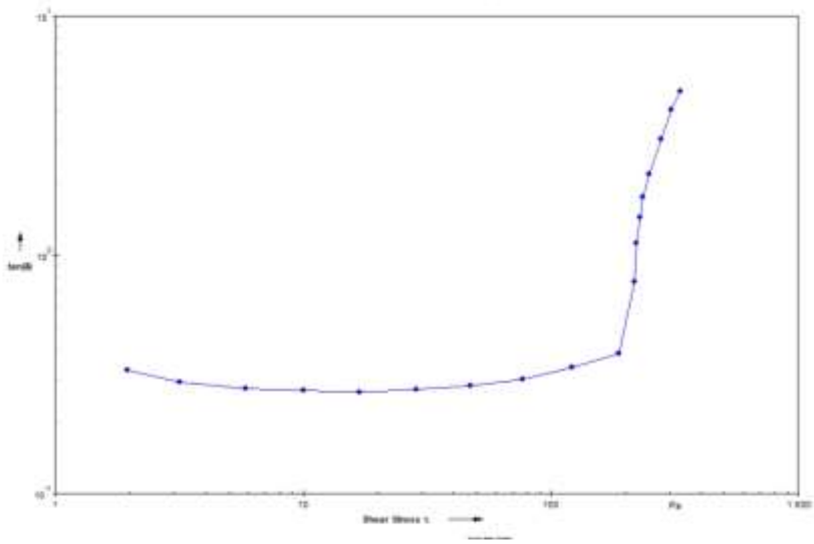

Figure 5 Example of measured viscoelastic properties of the superaborbent.

3. CONCLUSION

Novel superabsorbent composites for agricultural and environmental usage were developed and investigated. There were several samples with various composition compared. The result of our experiments showed that we are able to prepare superabsorbent polymers of various swelling behaviour. Storage modulus obtained from viscoelastic measurements indicated that an increase in swelling capacity led to a decrease in gel strength. Used sampes of superabsorbent polymers behave as viscoelastic solids. Because the polymer network is crosslinked, the gel network consists of one very large branched polymer which spans the entire gel. These samples exhibit huge potential to become one of the modern forms of fertilizer which can provide matrix for sustainable controlled release system.

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