SYNTHESIS, CHARACTERISTICS AND ANTIBACTERIAL ACTIVITY
OF POLYMERIC FILMS BASED ON STARCH AND POLYVINYL ALCOHOL

Sana K. Kabdrakhmanova¹, Esbol Shaimardan², Kydyrmolla Akatan²,
Ainur K. Kabdrakhmanova³, Nurgamit Kantai², Madi B. Abilev²

¹Satbayev University, 22 Satbayev str., Almaty
Republic of Kazakhstan,
E-mail: sanaly33@mail.ru
²S. Amanzholov East Kazakhstan State University,
18/1 Amurskaya str., Ust-Kamenogorsk
Republic of Kazakhstan
³I.Zhansugurov Zhetysu State University,
187а Zhansugurov str., Taldykorgan
Republic of Kazakhstan

ABSTRACT

The optimal composition based on polyvinyl alcohol (PVA) and starch in a combination with “Maxim” fungicide is developed for sunflower seeds encapsulation. It is achieved by varying the concentration and ratio of the polymers and fungicides used. The physico-mechanical characteristics of the obtained composites are identified. The laboratory and field germination, as well as the yield and infestation of sunflower seeds with fungal diseases are established.

Keywords: starch, polymer composite, sunflower, viscosity, germination.

INTRODUCTION

Today one of the main tasks of modern chemistry is to find a solution of the urgent problems of the agro-industrial complex. The main among them refers to the improvement of the agricultural crops quality and yield. One of the main conditions for the formation of an optimal crop yield pattern can be attributed to presowing seed treatment through encapsulation by various film-forming polymers in combination with various additives. This method allows using a system including seed disinfectants, growth regulators, other physiologically active compounds and the polymer itself, without exerting an increased load on the soil biota and the harvest-soil-atmosphere ecosystem. The method is of a great importance for oilseeds, sunflower in particular, whose growing is one of the agriculture leading branches in the Republic of Kazakhstan. One of the reasons for the low yield of sunflower culture is its susceptibility to various diseases during the growing season. Such diseases as phomosis, fomopsis, sclerotiniosis (white rot), gray mold, downy mildew appear at the early stages of sunflower development but continue to affect the crop till its maturation reducing the yield or destroying it. To avoid this plant mass contamination by harmful diseases, a large number of fungicides are used, which requires additional financial costs and, on the other hand, affect negatively the environment state. Aiming a full-scale development and release of the domestic sunflower oils to the world market, the researchers focus on the development of new technologies for preplant processing of sunflower seeds. This will ensure an increase in the seed quality, a decrease in the consumption of disinfectants used, and an increase of the seedlings resistance to pathogenic microorganisms. In this regard, the fungicidal activity of encapsulation is of particular relevance [1]. A composite of a pesticide and a polymer is proposed, where the acid groups of the polymer matrix (maleic acid-methyl vinyl ether copolymer, maleic acid-butyl vinyl ether copolymer, polyacrylic acid, polymethacrylate) form a hydrogen bond with the pesticide [2].
At present, intensive research is being carried out aimed at obtaining optimal encapsulating composites that are effective at minimally low rates of consumption while being biodegradable in natural environments providing toxicological and ecological safety. These factors require the production of composites based on raw materials, which can be biological polymers of plant origin. Carboxymethylcellulose, starch, gelatin, alginate, chitosan and others [3 - 10] are widely used polymers of the type. Of these, starch is non-toxic and highly biodegradable, it is relatively cheap and can be obtained from various easily renewable crops.

Furthermore, it can provide the preparation of biodegradable materials in combination with synthetic polymers. But its high hydrophilicity and low mechanical properties make it unsuitable for obtaining pure starch films [11, 12]. The prospects of obtaining biodegradable stable composites based on starch with other polymers are noted [13].

Films based on a mixture of PVA and starch for use in the field of biomedicine [14], in agriculture [15], etc. have been obtained. The use of PVA is due to the fact that it is a non-toxic, biodegradable, highly soluble in water. However, the high cost of PVA requires its use in a form modified by cheaper polymers depending on the field of application [16 - 21].

The aim of this work is to obtain the optimal encapsulating composition based on starch and PVA with inclusion of different fungicides and study their physicochemical properties and influence on the germination of sunflower seeds.

EXPERIMENTAL

Materials

We used PVA produced by Sigma-Aldrich with a molecular mass of 30,000 - 70,000 and a degree of hydrolysis of 87 % - 90 % and starch of “puriss” grade. PVA and starch were not subjected to additional purification.

“Maxim” is a contact fungicide. It is used for pickling flowers bulbs, other planting material (corms, seeds) from rotting before planting and during storage. Usually a single treatment is required. The period of protective action is 12 weeks. It is used in the form of a suspension. The concentration of its active component, fludioxonyl, is 25 g/L. This commercial product was chosen as a fungicide in the study presented.

Procedure for the preparation of an encapsulating composition

The encapsulating composition for seed coating was prepared as follows: the concentration of the initial polymers of PVA and starch varied from 1.0 and 7.0 % (by mass). The volumetric ratios of starch (0.5 - 5 %): PVA (5 %) were 1:1, 1:4, 4:1, 3:2 and 2:3, respectively. Solutions of “Maxim” fungicide of concentrations of 1.0 %; 5.0 % and 10.0 % were used. To obtain encapsulating films, starch:PVA:”Maxim” solutions of varying components ratios were applied to a plastic surface. The films were formed through irrigation and subsequent distribution over the surface with a special “scraper” device with a gap of 1 mm providing uniform distribution of the solution and hence a uniform thickness of the film formed. The drying time of the films was 5-10 h. Sunflower seeds were treated with solutions of polymers of optimal concentrations in combination with fungicides of different concentrations. After processing, the seeds were dried and seeded in triplicate (5 seeds in each well).

Methods

The study of the polymers rheological properties was carried out on an automatic viscometer of Ubbelohde brand with a measurement accuracy of ±0.1 %. To analyze the rheological properties, solutions of polymers samples of different concentrations (0.5 % - 6 %) were prepared in deionized water. The solutions were left overnight at 4°C. The next day, the samples were stirred at room temperature until the polymers were completely dissolved. Then, samples of 20 mL were taken from the solutions. They were heated to 100°C, stirred for 5 min. and subsequently cooled to 25°C.

The structure and morphology of the polymer composites based on PVA and starch was studied by scanning electron microscopy (SEM). A low-vacuum scanning electron microscope JSM-6510LA combined with an energy-dispersive X-ray spectrometer (“JEOL”, Japan) with an accelerating voltage of up to 30 kV was used. The resolution was up to 3.0 nm, while the magnification was up to 300,000.

The mechanical properties of the resulting films, including tensile strength and elongation, were measured at room temperature on Zwick/RoellZ 0.5 under the following conditions: the grip distance was 20 mm, the preload on the sample was 1 H, the preload rate was 10 mm/min, the test rate was 50 mm/min. The thick-
ness of the samples was measured using «INFINITER IN CO». The range of the thickness measurement was 0 - 1250 μm, the accuracy was 3 %, while the resolution was 0.1 μm.

The films solubility in water was determined according to the procedure described in [3]. Optimal film-forming compositions from starch and PVA in combination with fungicides were selected for the study.

The mycological characteristics were determined by the microscopic method of «levenhuk C510NG». The magnification was in the range from 40 to 2000, the resolution was 5.1 times, while the sensitivity was 1/2.5.

The germination of encapsulated sunflower seeds was determined in accordance with GOST 12038-84 (GOST 12038-84. Seeds of agricultural crops. Methods for determination of germination // M.: Standard-Form., 2011. - P. 64).

Small-scale vegetation experiments were carried out on the basis of East Kazakhstan Research Institute of Agriculture (EKRIA), the department of oilseeds, on an area of 2 hectares. The sowing was conducted on May 18, 2016 (in 2015 the crop was also sowed on May 18), when the soil at the depth of the seeding (6 - 8 cm) warmed up to the desired temperature (12 - 14°C). The experimental field was divided to tiers, and the tiers to plots. Field labels were arranged along the tier, while numbering was made according to the test schemes. The sowing of the experimental plots was carried out manually, with sandwich-popppers. The sowing scheme was 70 x 35 cm, 3 - 5 seeds per nest.

To determine the yield, the harvested crop from the plot was weighed and samples were taken at the same time to determine their moisture content. An average sample was collected for carrying out laboratory analyses (1000 seeds, kernel and seed oil, and husk) and determining the percentage of purity. The yield was determined on the ground of the formula:

$$\text{Yield} = \frac{\text{net weight of seeds} \cdot \text{number of plants} \cdot S_{\text{count}}}{\text{number of harvested baskets}}$$

RESULTS AND DISCUSSION

To obtain capsules with walls of uniform thickness, it is necessary to prepare a solution of a certain viscosity. The viscosity of the solutions depends on many conditions, such as the composition of the solution, the concentration of the components, the temperature of the solution, the pH of the medium, the presence of electrolytes in the solution, and also the conditions of preparation. In order to make a recipe for the preparation of polymer solutions of optimal characteristics, it is necessary to study the viscosity of aqueous solutions of individual components. Using the Mark-Kuhn-Hauving equation, the molecular weight of the polymers is found. Fig. 1 shows the curves of the conditional viscosities of PVA and starch at different concentrations.

According to the obtained data, the average value of the outflow time of PVA solution is 1015.77 s. For starch, this value is found equal to 362.80 s. For PVA, the maximum viscosity increase with the formation of a viscous gel occurs already at a concentration of 4.0 %, while the conditional viscosity rapidly increases approximately twofold, i.e. from 5 s to 11 s (Fig. 1). A sharp increase in starch viscosity is observed at a con-

![Fig. 1. Viscosity of PVA at various concentrations.](image)

![Fig. 2. Nominal viscosity of starch at different concentrations.](image)
centration of 3 % (Fig. 2). Summarizing the established dependence of the viscosity of PVA and starch in the higher concentrations region, it can be assumed that an increase in the polymers concentration of more than 4 - 5 % for PVA and 3 % for starch will lead to a sharp increase in viscosity, and consequently make them unsuitable for film formation by irrigation (Figs. 1 and 2). Consequently, under the experimental conditions, we were unable to obtain film-forming solutions of PVA and starch with the flow expected at concentrations above these values. The molecular masses of PVA and starch were 402,580 g/mol and 403,840 g/mol, respectively. According to the data obtained, the optimal concentration of PVA for films formation is in the interval of 4 - 5 %, while for starch it ranges from 1 to 3 %.

Fig. 3 shows encapsulating films based on starch (1%):PVA (5%) in ratios of 1:1; 2:3; 3:2 and 1:4. According to the data obtained, not all polymer films proved to be acceptable for encapsulation of sunflower seeds (Figs. 3, 4).

Qualitative polymer films are obtained introducing “Maxim” fungicide to starch (1 %):PVA (5 %) in ratios of 1:1 and 1:4, respectively. The resulting films were transparent and flexible enough, so they folded easily in half. Their average thickness, rupture strength and elongation were established starch (Table 1).

There is a slight increase in strength at break and elongation with the addition of the “Maxim” fungicide. In general, it can be concluded that the fungicide and its concentration do not particularly affect the strength characteristics of the polymer films based on starch and PVA.

Scanning electron microscopy was used to study the surface image and chemical composition of the resulting polymer composites (Figs. 5 - 7).

The obtained SEM data of the encapsulating com-

<table>
<thead>
<tr>
<th>Designation of samples</th>
<th>Average thickness, μm</th>
<th>Breaking strength, MPa</th>
<th>Relative extension, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch (1%): PVA (5%) (1:1)</td>
<td>26.53</td>
<td>30</td>
<td>32</td>
</tr>
<tr>
<td>Starch (1%): PVA (5%) (1:1) / 5% Maxim</td>
<td>27.9</td>
<td>31</td>
<td>32</td>
</tr>
<tr>
<td>Starch (1%): PVA (5%) (1:1) / 10% Maxim</td>
<td>28.6</td>
<td>31</td>
<td>33</td>
</tr>
</tbody>
</table>
position of starch (1%) : PVA (5%) (1:1) shows that it is characterized by a uniform surface of no lumps and damages. Unreacted substances are seen at several spots. Aluminum, silicon and lead are found in trace amounts (Figs. 6 - 7). The polymer film mainly consists of carbon (69.7 %), oxygen (28.66 %), sodium (0.70 %), and other elements.

The results referring to the determination of the solubility of the optimum films in water are shown in Figs. 8 - 9. It is seen that the solubility of films without a fungicide increases with time and reaches equilibrium about an hour later. Samples of these films decompose in water into small pieces with the formation of a uniform sediment. This pattern of dissolution in water is preserved with the use of “Maxim” fungicide as well (Fig. 9). An increase in the composites solubility is observed. Perhaps this is because the etchant belongs to the soluble part of this composite and, when dissolved in water it affects the polymer structure by destroying the cross-linking.

The formation of a new system of hydrogen intermolecular bonds at the stage of obtaining films from starch and PVA, as well as amylose, hampers water molecules diffusion in view of the crosslinks in the starch molecule. This in turn determines that PVA is the soluble part of the films. In fact the iodine indicator for starch shows a negative result.
The optimum polymer composites containing starch:PVA ratios of 1:1 and 1:4, respectively, and “Maxim” fungicide at a concentration of 5 % and 10 % are tested in preliminary laboratory and field experiments to determine the germination of sunflower seeds. All necessary biological and agronomical characteristics of the crop were determined in the field experiments. For seed encapsulation, a hybrid sunflower seed “Kazakhstan 2011 F1 465” was selected and taken from the oilseeds department of the EKSRIA. Seeds of this sunflower sort were encapsulated by the optimum polymer composites pointed above.

The seed germination results obtained under laboratory conditions are shown in Table 2 and in Figs. 10 - 11. The control experiment shows high germination of 46.2 %, while the amount of not germinating seeds is 38.15 % (Table 2, Fig. 11). It should be noted that a relatively good increase in sunflower seeds with a starch composition (1 %) is observed in case of “Maxim” fungicide of different concentrations (5 % and 10 %) under controlled conditions: PVA (5 %) (1:4)/Maxim 10% (Fig. 11). Germination is high - 97.48 %, while not germinated seeds - 2.52 %. The data in Table 2 shows that an increase in the concentration of “Maxim” fungicide promotes an increase in germination, thereby decreasing the number of sprouted but sick sunflower seeds. Given this fact, it can be concluded that 5 % and 10 % solution of “Maxim” fungicide is acceptable for the destruction of fungal diseases under controlled conditions.

Investigations are conducted to determine the field germination of seeds encapsulated seeds (Table 3).

Field germination is characterized by the following data: germination is 94.4 % when using a polymer composite: starch 1 %: PVA 5 % (1:4) + “Maxim” (10 %), while there is no amount of non-germinating seeds (Table 3). The composite containing 10 % of “Maxim”

Table 2. Effect of encapsulating compositions based on starch and PVA on laboratory germination of sunflower seeds.

<table>
<thead>
<tr>
<th>#</th>
<th>Samples</th>
<th>High germination, %</th>
<th>Not germinated, %</th>
<th>Germinated, but sick, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Control experiment</td>
<td>46.2</td>
<td>38.15</td>
<td>15.65</td>
</tr>
<tr>
<td>2</td>
<td>Starch 1%: PVA 5% (1:4) / &quot;Maxim&quot; (10%)</td>
<td>97.48</td>
<td>2.52</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Starch 1%: PVA 5% (1:4) / &quot;Maxim&quot; (5%)</td>
<td>78.88</td>
<td>19.86</td>
<td>11.89</td>
</tr>
<tr>
<td>4</td>
<td>Starch 1%: PVA 5% (1:1) / &quot;Maxim&quot; (10%)</td>
<td>71.42</td>
<td>16.18</td>
<td>12.4</td>
</tr>
<tr>
<td>5</td>
<td>Starch 1%: PVA 5% (1:1) / &quot;Maxim&quot; (5%)</td>
<td>64.74</td>
<td>19.86</td>
<td>15.4</td>
</tr>
</tbody>
</table>
Fig. 10. Germination of control samples (Sort of sunflower «Kazakhstan 2011 F1. 465»).

Fig. 11. Germination of sunflower seeds in presence of the encapsulating films of a composition: a, c - Starch (1%) + PVA (5%) (1:1): Maxim (10%); b, d - Starch (1%) + PVA (5%) (1:1): Maxim (5%).

Table 3. Effect of encapsulating compositions on the basis of starch and PVA on field germination of sunflower seeds.

<table>
<thead>
<tr>
<th>#</th>
<th>Samples</th>
<th>High germination, %</th>
<th>Not germinated, %</th>
<th>Germinated, but sick, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Control experiment</td>
<td>48.23</td>
<td>32.88</td>
<td>18.89</td>
</tr>
<tr>
<td>2</td>
<td>Starch 1%: PVA 5% (1: 4): &quot;Maxim&quot; (10%)</td>
<td>94.44</td>
<td>-</td>
<td>5.56</td>
</tr>
<tr>
<td>3</td>
<td>Starch 1%: PVA 5% (1: 4): &quot;Maxim&quot; (5%)</td>
<td>69.67</td>
<td>17</td>
<td>13.33</td>
</tr>
<tr>
<td>4</td>
<td>Starch 1%: PVA 5% (1: 1): &quot;Maxim&quot; (10%)</td>
<td>87.78</td>
<td>5.56</td>
<td>6.66</td>
</tr>
<tr>
<td>5</td>
<td>Starch 1%: PVA 5% (1: 1): &quot;Maxim&quot; (5%)</td>
<td>82.22</td>
<td>5.56</td>
<td>12.22</td>
</tr>
</tbody>
</table>
and PVA 1:1 shows field germination of 87.78 %, not germinated seeds presence - 5.56 % and presence of germinated, but sick seeds - 6.66 % (Table 3). The decrease of Maxim fungicide to a concentration of 5 % in the identical starch/PVA system results in germination of 82.22 %, and germinated, but sick seeds - 12.22 %. It should be noted that in the control experiment the seed germination is 48.23 % with germinated, but sick seeds - 18.89 % (Table 3). It is evident that the polymers type and concentration used for presowing treatment of the sunflower seeds influence the fungicides effect.

The yield of sunflower seeds encapsulated by polymers based on PVA and starch is determined, in comparison with the control samples yield.

$$Yield = \frac{0.43 \times 189}{52} = 997.2 \text{ kg/ha} = 9.97 \text{ c/ha}$$

0.43 kg - net weight of non-encapsulated seeds;
189 - $S_{count}$ coefficient;
52 - number of harvested baskets.

$$Yield = \frac{0.454 \times 1052.9}{52} = 1052.9 \text{ kg/ha} = 10.53 \text{ c/ha}$$

0.454 kg - net weight of encapsulated seeds;
1052.9 - $S_{count}$ coefficient;
52 - number of harvested baskets.

The effect of the encapsulating composition on the growth, development and yield of sunflower under field conditions is given in Table 4. The table gives values from 3 replicates of 65 plants. According to the data obtained, the yield of encapsulated seeds is 10.53 c/ha, with a control experiment of 9.97 c/ha (Table 4).

It follows from the results obtained that the polymer composite containing starch 1 %: PVA 5 %: “Maxim” significantly improves sunflower growth and development, which leads to its yield increase, primarily by increasing the density of plant standing due to the earlier more favorable seedling shoots.

Studies were carried out to follow the effectiveness of decontamination of sunflower seeds by the polymer composites developed. The results show that the highest occurrence of control seeds of sunflower (laboratory germination) is noted in presence of Alternaria pathogens, an average of 15.65 % (Table 5).

It was established that the infection of sunflower seeds after encapsulation by composites containing «Maxim» fungicide decreases to 2.21 %. In some cases, complete absence of affected seeds is observed (Table 5). In average, under controlled laboratory conditions, the incidence of seeds is from the total absence of fungal disease to 15.65 %. Mycological analysis of sunflower grown in the field finds the presence of pathogens of species: Alternaria, and Sepedonium chrysospeimum in Botrytis cinerea cells. It is established that under

<table>
<thead>
<tr>
<th>Samples</th>
<th>Laboratory results</th>
<th>Field results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Seed germination,%</td>
<td>Seed damage,%</td>
</tr>
<tr>
<td>Control</td>
<td>46.2</td>
<td>15.65</td>
</tr>
<tr>
<td>Starch (1%) + PVA (5%) (1:1): 5% Maxim</td>
<td>64.74</td>
<td>15.4</td>
</tr>
<tr>
<td>Starch (1%) + PVA (5%) (1:1): 10% Maxim</td>
<td>71.42</td>
<td>12.4</td>
</tr>
<tr>
<td>Starch (1%) + PVA (5%) (1:4): 5% Maxim</td>
<td>78.88</td>
<td>11.89</td>
</tr>
<tr>
<td>Starch (1%) + PVA (5%) (1:4): 10% Maxim</td>
<td>97.48</td>
<td>-</td>
</tr>
</tbody>
</table>
the field conditions the polymer composites containing starch (1\%): PVA (5\%) in a ratio of 1 to 4 as well as 5\% or 10\% of Maxim are effective against fungal pathogens (Table 5).

Thus, the data of phytosanitary research leads to the conclusion that capsulation of seeds by polymeric composites based on PVA and starch, in combination with fungicide Maxim, increases laboratory and field germination to 97.48\% and 94.44\%, respectively (Table 5). The optimal composite, positively influencing sunflower seeds germination both in laboratory and field conditions is the one containing starch (1\%) + PVA (5\%) (1:4): 10\% Maxim.

**Fungicidal tests**

The results of the study show the highest occurrence (about 15.65\%) of the pathogens of Alternaria in control seeds of sunflower (laboratory germination, Fig. 12). These data is confirmed by the results of the microscopic examination (Fig. 13).

Fungi of this genus have multicellular darkly colored conidia with transverse and longitudinal septa. The form of conidia is diverse and represents variations in the shape of the ovoid type. The upper end of the conidia is extended into a short or long “spout”. In many alternatives, conidia form easily disintegrating chains. However, among the alternatives there are representatives with solitary conidia, in which the “nose” is usually extended into a long thread. Conidiophores are always dark-colored, simple or at the apex, stepped-bent.

It is found that the infection of sunflower seeds...
after encapsulation by composites with the addition of fungicides decreases down to 2.21 % (Fig. 14). In some cases, complete absence of affected seeds is observed. In average, under control laboratory conditions, the damage of seeds ranges from total absence of fungal disease to 11.068 %.

Mycological analysis of sunflower grown in the field provide to identify the presence of pathogens of Alternaria, and Sepedonium chrysospeimum species in Botrytis cinerea cells (Fig. 15).

CONCLUSIONS

An optimal composition based on PVA and starch in presence of “Maxim” fungicide is developed to encapsulate sunflower seeds. It affects positively seed germination as well as formation and development of sunflower seedlings. It is found that an increase in PVA concentration above 4 - 5 % and that of starch above 3% results in a sharp increase in viscosity, thus making them unsuitable for film formation by irrigation. Optimal encapsulation is achieved using composites containing starch (1 %): PVA (5 %) in the ratios of 1:1 and 1:4 and “Maxim” fungicide (5 %, 10 %).

Acknowledgements

The study was supported by the Ministry of Education and Science of the Republic of Kazakhstan (Project #1916/GF4).

REFERENCES


15. Z. Zhu, R. Zhuo, Slow release behavior of starch-g-poly(vinyl alcohol) matrix for 2,4,5-trichlorophenoxyacetic acid herbicide, European Polymer Journal, 37, 2001,1913-1919.


