Characterization of blend and composites for agricultural use at arid and semi arid soils

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ABSTRACT

The use of polymers as soil-stabilizer additive has expanded significantly in agricultural use to control soil degradation, desertification and to improve arid and semi arid soils. This research was conducted to determine the effects of different synthetic polymers and biopolymers at low concentration (0.03 %-1%) at arid and semi arid soil of North Africa. Polystyrene (PS), Polyacrylamide (PAM), Cellulose and the mixture of PAM and PS were characterized by viscosity, infrared spectroscopy, X-ray Diffractometry, thermal analysis (TG and DSC) and Scanning electron micrographs (SEM). The results showed that composites from polymers: PAM and PS with Cellulose in soil, could improve better, soil physical proprieties and augment water retention at arid soils compared with application of any other polymers at the same concentrations. This work can help to improve the productivity of arid and semi arid soils by using low concentration of biopolymers from plant fibers and polymers from synthetic plastics compounds or the wastes of plastic industry, aiming the increase of water holding capacity and also to improve physical properties of soils by binding soils particles together. The reduction of the water loss; also to make valuable wastes of plastic industry and renewable organic fibers to protect environment.

Key words: Composites, Polymer, Polyacrylamide, Polystyrene, Arid and semi arid Regions, Cellulose, Biopolymers, Wastes.

Abbreviations: (PAM) - PolyAcrylamide; (Cell)- Cellulose; (PS)- Polystyrene; (V/V)- volume to volume.

INTRODUCTION

Arid and semi arid soil are characterized by low erratic rainfall and long periodic droughts, high evaporation level. Soil degradation threatens water quality and agricultural productivity through the loss of valuable top soil. Polymers and biopolymers have long been recognized as viable soil conditioners, because they stabilize soil surface structure and pores continuity.

In the past decade water soluble polymers was identified as a high effective erosion preventing and infiltration enhancing polymers, (Lentz et al, 1994).

Polyacrylamide was effective in enhancing the stability of soil aggregates (Steven Green et al, 2004) and increase soil infiltration in some areas especially in sandy loam soils (Steven Green et al, 2000; Hussein and Thomas, 2006). Polyacrylamide is a long-chain synthetic polymer that acts as a strengthening agent, binding soil particle together and holding soils in place, but Polyacrylamide alone not remediate poor soil Structure, (Cook and Nelson, 1986).
Acid - hydrolyzed Cellulose micro fibrils alternative to Polyacrylamide for soil stabilization was tested and show promises (Orts et al, 2007). The general objective of this study was to produce a series of low costs polymers and biopolymers to quantify their effectiveness on soil retain water, decrease evaporation; improve soil aggregate stability and other structural properties.

The present work tends to make valuable products of plastics wastes (Polystyrene) and synthetic compounds (Polyacrylamide) with Cellulose and soil as a composite materials to retain water and humidity for crops and plants at arid and semi arid regions.

The uses of Polyacrylamide-Cellulose blend appears promising for reducing the cost of irrigation at arid and Semi-arid soils, and offer a safe environmentally friendly, inexpensive materials. The environmental advantages of degradable sources may give the Cellulose Alfa-Alfa economic advantages, as a source of polysaccharides to arid soils that generally lack structural polysaccharide; also Cellulose Alfa-Alfa. (Stipa tenacissima) is very rich plant in Cellulose fibre, also it resist very well to drought at semi arid regions, in the same time it’s annually renewable and its additions would generally be regarded as environmentally beneficial. Polystyrene used as impermeable subsurface layer barrier for water movement during irrigation or rainfall provide also deep percolation of water.

**EXPERIMENTAL**

**Material and Methods**

Styrene (Aldrich 99 %), Acrylamide was supply by (E.MERCK) was purified by crystallisation and recrystallisation in hot methanol; crystals are separated by filtration then desiccated under vacuum at 30 C°.

Also we purified Potassium persulfate as the same manner.

Water used as solvent was bidistilled water at KMnO₄.

Methanol 215 (Romil-SPS 99.9 %), ethyl benzene (Carlo Erba, chimica Milano), Toluene (BDH chemical LTD)

Acetone (Romil-SA), Potassium persulfate (99.9 %) and Benzoyl peroxide (98 %) (Sigma - Aldrich). All other reagents were used as received.

**Extraction of Cellulose from Alfa-Alfa plant**

The cellulose was extracted from alpha plant with toluene/ethanol mixture (2/1, V/V) for 6 hours in Soxhlet apparatus and treated with NaOH (1M) for 8 hours at 25°C (Shigemasa et al, 1990; Heinz et al, 2000).

**Table 1: Synthetic details of blend and composites (polymers with soil)**

<table>
<thead>
<tr>
<th>Sample N°</th>
<th>Soil type (50g)</th>
<th>Cellulose (%)</th>
<th>Polycrylamide (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Arid</td>
<td>0.5g/l (1% )</td>
<td>15 mg/l (0.03% )</td>
</tr>
<tr>
<td>2</td>
<td>Arid</td>
<td>0.5g/l (1% )</td>
<td>0 mg/l</td>
</tr>
<tr>
<td>3</td>
<td>Arid</td>
<td>0 g/l</td>
<td>15 mg/l (0.03% )</td>
</tr>
<tr>
<td>4</td>
<td>Semi Arid</td>
<td>0.5g/l (1% )</td>
<td>15 mg/l (0.03% )</td>
</tr>
<tr>
<td>5</td>
<td>Semi Arid</td>
<td>0.5g/l (1% )</td>
<td>0 mg/l</td>
</tr>
<tr>
<td>6</td>
<td>Semi Arid</td>
<td>0 g/l</td>
<td>15 mg/l (0.03% )</td>
</tr>
</tbody>
</table>

**Table 2: Physical and chemical proprieties of arid soils (0-20cm)**

<table>
<thead>
<tr>
<th>S %</th>
<th>(C + Si) %</th>
<th>CaCO₃</th>
<th>EC (mS/cm)</th>
<th>MO %</th>
<th>CEC (meq/100g Soil)</th>
<th>PH</th>
<th>Soil textural class</th>
</tr>
</thead>
<tbody>
<tr>
<td>74.52</td>
<td>25.48</td>
<td>5.17</td>
<td>0.23</td>
<td>0.50</td>
<td>3.2</td>
<td>7.84</td>
<td>Sandy</td>
</tr>
</tbody>
</table>
Fig. 1: Reduced $\eta$ versus concentration of PAM

Fig. 2: Reduced $\eta$ versus concentration of PS

Fig. 3: FTIR spectrum of Cellulose fibres with KBr

Fig. 4: FTIR spectrum of (PAM) film

Fig. 5: FTIR spectrum of (PS) film

Fig. 6: FTIR spectrum of arid soil with (Polyacrylamide + Cellulose) with KBr
Preparation of Polyacrylamide (PAM)
For the polymerisation reaction we used the method proposed by Schultz (Schultz et al., 1959).

Polyacrylamide was prepared by radical polymerisation in aqueous solution with acrylamide as monomer.

(8g dissolved in 260 ml of bidistilled water), potassium persulfate $K_2S_2O_8$ (0.4g dissolved in 10 ml of distilled water) as initiator, the reaction lasted for 5 hours at constant temperature under inert anhydride nitrogen.

Vigorous stirring ensured homogeneous conditions by RW 20 IKA-WERK motor.

The polymer solution obtained was concentrated by “Rota vapor” (1/3 of initial volume), then it precipitated in methanol (V/V, 1/7) and filtered at Buchner.

The obtained Polyacrylamide was cleaned by dissolved it in bidistilled water then precipitated second time in methanol to eliminate all initiator and monomer traces, then filtered at Buchner, desiccated using inert nitrogen atmosphere (anhydride $N_2$) under vacuum at 30°C.

Preparation of Polystyrene (PS)
Polystyrene obtained by radical polymerisation at constant temperature 60°C; we used benzoyl peroxide as catalyst and toluene as a solvent:

In reactor contain styrene and toluene solution ($V_{\text{styrene}}$/$V_{\text{toluene}}$, 1/3) immersed in thermostat bath at 60°C we added slowly benzyl peroxide ($10^{-3}$mol/l dissolved in 10 ml of toluene); the reaction lasted for 8 hours at constant temperature under inert anhydride nitrogen and continuous stirring.

The polymer solution obtained was concentrated to (1/3 of initial volume), then it
precipitated in methanol (V/V, 1/7) and filtered at Buchner, The solid obtained rinsed with methanol.

**Molecular weight of Polyacrylamide and Polystyrene by Viscosimetry**

The viscosity measurements of diluted solutions of polyacrylamide and polystyrene were carried out in a capillary Ubbelohde viscometer 75 in a LAUDA CD 15 bath. The flow times were measured with accuracy of ± 0.01 S. from the efflux time measurement, the specific viscosity ($\eta_s$) was calculated at different concentration. The intrinsic viscosity [$\eta_I$] was determined by plotting reduced viscosity [$\eta_s/C$] against the solutions concentrations (C) according to the well known MARK-HOUWINK relation $[\eta] = KM^{\alpha}$, where K and $\alpha$: are constants for a given polymer/solvent/ temperature system, Viscosity of Polyacrylamide was determined in bidistilled water at 30°C, the value of $K = 0.65 \times 10^{-2}$ and $\alpha = 0.82$ and Viscosity of Polystyrene was determined in Ethyl benzene with $K= 17.6 \times 10^{-3}$ and $\alpha = 0.68$ at 25°C (Polymer Data Handbook 1999).

**Preparation of blend and composites polymers**

Polymer blending provides a relatively facile means of combining the separate desirable proprieties of different polymers into a single material.

Blends were prepared using solution routes and physical mixing (the latter for DSC measurements only)

Different compositions of Polyacrylamide (PAM) and Cellulose are prepared in wide composition range by solution mixing:

A-(Polyacrylamide-Cellulose) blend was prepared by dispersing Cellulose fibres in Polyacrylamide solution was sonicated for various times between 10 and 15 minutes using ultrasonic, dispersion increased with sonication time and times
in excess of 15 minutes apparently resulted in the dispersion of cellulose fiber.

B- (Polycrylamide- Cellulose) Mixture by dispersing Cellulose fibre in acetone solution then we added Polyacrylamide solution with continuous stirring.

C- Simple mixing of Polyacrylamide solution and Cellulose with continuous stirring.

We prepared different blend of Polyacrylamide and Cellulose, using (0 mg/L -20 mg/L) of Polyacrylamide concentration and Cellulose concentration from (0 g /L - 0.5 g/L).

**Preparation of Polystyrene sub layer**

Polystyrene film was prepared using the same method used by IKEJIMA et al, 2000; (9) Olabarrieta et al, 2001). We used the casting method (wet method) to prepare Polystyrene film; the thickness of polystyrene film can be controlled by polymer concentration:

We prepared 2- 4 % (w/w) of Polystyrene film by dissolving 5-10 g of polystyrene in 250 ml of toluene under continuous stirring (300 rpm); after filtering the polymer was cast at temperature between 50-60°C then removed from the mould and stocked at 23 ±2 °C.

**Thickness of sub layer film**

The thickness of sub layer film was measured at 3 different points with 0.1ìm precision using micrometer (Twing -Albert instrument Co., Philadelphia, USA).
Soil Specimen preparation

Two soils from Algeria were chosen for this study: arid soil from Biskra (Ain Benoui) and semi-arid soil from Batna (Merouana) samples of the soils were taken from the Surface layer (0-20 cm) and were analyzed using standard analytical methods (Klute, 1986; page et al., 1982), selected physical and chemical proprieties of the soils are given in Table 2.

Specimen treated with different biopolymers and polymers Mixtures concentrations. We sprayed Polyacrylamide-Cellulose blend and composite at arid and semi-arid soil surface.

Water-retaining property

50g of arid and semiarid soil treated with a different amount of polymers (Polyacrylamide and Cellulose), was put in plastic container (6 cm in diameter, 7 cm in depth) similar to Polystyrene sub-layer to avoid loss of water by deep percolation. Then 20 ml tap water was poured into the container. All container were placed on simulator of temperature and wind at 30°C and 1.2 bars during day, and placed on tables in a constant air-temperature Room (25°C, air relative humidity 20 %) during night, to simulate desert conditions, the water content of each soil sample was determined by taking a small sample from the container every 24 h, oven-drying at 105°C for 24 h and determining weight loss:

\[
\text{Water content (\%)} = \frac{\text{wet soil weight} - \text{dry sol weight}}{\text{wet soil weight}} \times 100
\]

Characterisation

Polymers and composites were characterized by elemental analysis: IR spectroscopy, thermal analysis, scanning electron micrographs (SEM), and X-ray diffractometry (XRD).

Elemental analysis

To determine the organic, mineral and dry matter of Alfa-Alfa plant we used the elemental analysis.

FTIR analysis

FTIR spectra were recorded on Perkin-Elmer- Paragon 500 FT-IR spectrophotometer in the range 4000 - 400 cm⁻¹. Using thin film by solution casting via air evaporation and KBr, the thin films were prepared by casting polymers solutions on glass plates.

Thermal analysis

Thermal analysis was carried out with Mettler TATC 11 thermal analyser.

Both thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) of all samples were performed up to a temperature of 600 °C, starting from room temperature in nitrogen atmosphere. A heating rate of 10° / min was maintained in all cases and flow rate of 30 ml / min nitrogen.

X-ray diffractometry (XRD)

Polymer samples were subjected to XRD analysis, the powdered polymer sample was packed
into a hole of 2 mm diameter in a small container made of perpex about 1, 5 mm thick A PW 1830 diffract metre and P3020 X- Ray generator (Phillips, Holland) Were used for this study producing CuKα radiation, the scattering angle (2θ) was varied from 10 to 45 °.

**Scanning electron microscopy (SEM)**

SEM micrographs were taken using Philips XL20 (Philips analytical Inc., the Netherlands). Samples was coated by gold before examination (cathode dispersion).

**RESULTS AND DISCUSSION**

**Soils analysis**

Table 2. Physical and chemical proprieties of arid soils (0-20cm)

<table>
<thead>
<tr>
<th>S</th>
<th>Sand, C</th>
<th>Clay, Si</th>
<th>Silt, CaCO₃</th>
<th>total carbonate, EC</th>
<th>electrical conductivity, MO</th>
<th>organic matter content, CEC</th>
<th>cation exchange Capacity, CO</th>
<th>Coarse, CO.S</th>
<th>Coarse Sand</th>
<th>CO.Si</th>
<th>Coarse Silt</th>
<th>f</th>
<th>fine, f.S</th>
<th>fine sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>S; Sand, C; Clay, Si; Silt, CaCO₃</td>
<td>total carbonate, EC</td>
<td>electrical conductivity, MO</td>
<td>organic matter content, CEC</td>
<td>cation exchange Capacity, CO</td>
<td>Coarse, CO.S</td>
<td>Coarse Sand</td>
<td>CO.Si</td>
<td>Coarse Silt</td>
<td>f</td>
<td>fine, f.S</td>
<td>fine sand</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Clay soil had higher amount of organic matter content than sandy soil.

**Elemental analysis**

From 2g of Alfa plant we can obtain: Dry material = 1.885 g, mineral matter = 1.22 %, organic matter = 17.78 %.

**A Viscosimetry Molecular weight of Polyacrylamide**

Polyacrylamide Viscosimetry Molecular Weight, $M_v = ([η]/K)^{1/α} = 104758.93 \text{ g/mol}$, Polymerisation degree: $DP = 104758.93/71.08 = 1473.81$

**B Viscosimetry Molecular weight of Polystyrene**

Polystyrene Viscosimetry Molecular weight, $M_v = ([η]/K)^{1/α} = 142992.2 \text{ g/mol}$, Polymerisation degree: $DP = 142992.2/104.14 = 1373$

**Melting point**

Melting point was measured with capillary tube using: Barnstead-Electro thermal apparatus. Polyacrylamide Melting point was: $T_f = 161\degree C$
IR Spectra

From the IR spectra of Cellulose it is evident that it shows a broad absorption band at 3274 cm\(^{-1}\) (stretching frequency of the OH group), 2914 cm\(^{-1}\) (C-H stretching vibration) 1429 cm\(^{-1}\) are assigned to CH\(_2\) vibration, 1160 cm\(^{-1}\) (cycle vibration).

In the case of PAM a broad absorption band at 3360 cm\(^{-1}\) is for NH group, two strong bands around 1670 cm\(^{-1}\) and 1633 cm\(^{-1}\) are due to C=O and NH, 1724 cm\(^{-1}\) free acid group, 1398 cm\(^{-1}\) and 2930 cm\(^{-1}\) are for C-N and C-H vibrations, 1449 cm\(^{-1}\) (CH\(_2\) group). In the case of Polystyrene:

characteristic IR absorption bands:

- An absorption band at 3028 cm⁻¹ and 3061 cm⁻¹ is for (\(=\) C-H) aromatic group.
- 2924 cm⁻¹ vibration of C-H.
- 1595 cm⁻¹ vibration of (-C = C-) liaison.
- 1494 cm⁻¹ vibration of C-H.
- The deformation vibration of (C-H) appears at 757 cm⁻¹.

From the IR spectra of arid soil treated with (Polyacrylamide + Cellulose), it is evident that it shows absorption bands from 659-1000 cm⁻¹ (C=C-H bending), bands from 1008.8-11842 cm⁻¹ (C-O, C-N stretching), bands from 1427.2-1473.5 cm⁻¹ indicated the presence of (C-H bending), the bands from 1620.1-179.6 cm⁻¹ (C=O, C=N, C=C stretching), band at 3242.1 cm⁻¹ due to OH group, band from 3487.1-3404.1 cm⁻¹ due to (N-H group), we can see OH free group at 3544.9-3616.3 cm⁻¹. From the IR spectra of semi-arid soil treated with (Polyacrylamide + Cellulose): absorption band at 3622.1 cm⁻¹ (C-O, C-N, C=C stretching), band at 3242.1 cm⁻¹ due to OH group, band from 3487.1-3404.1 cm⁻¹ due to (N-H group), we can see OH free group at 3544.9-3616.3 cm⁻¹. From the IR spectra ofsemi-arid soil treated with (Polyacrylamide + Cellulose): absorption band at 3622.1 cm⁻¹ (C-O, C-N, C=C stretching), band at 3242.1 cm⁻¹ due to OH group, band from 3487.1-3404.1 cm⁻¹ due to (N-H group), we can see OH free group at 3544.9-3616.3 cm⁻¹.

The results of IR spectrum of arid and semi-arid soil indicated that the soils are composites consisting of Cellulose and the polymerized Polyacrylamide solution.

Thermal analysis

**A-Thermo gravimetric analysis TGA**

Before studying the thermal effects on these polymers, thermal stabilities and degradation patterns were determined by employing TG and DTA.

To examine the thermal stability of Polyacrylamid, Polystyrene and Cellulose Alfa-Alfa, Thermo gravimetric analysis Data under nitrogen flow were obtained: Cellulose showed initial weight loss at 70 °C is due to the presence of small amount of moisture in the sample, the second loss is due to the loss of CO₂ and the rate of weight loss increased with increase in temperature till degradation at 350 °C.

In case of PAM: the initial weight loss is followed by a continuous weight loss with increasing temperature, the PAM decomposes in 2 stages, the polymer starts to degrade at 270 °C followed by a second stage commencing at 390 °C degradation is due to the loss of the NH₂ group in the form of ammonia. The TGA curve of Polystyrene: the first weight loss is due to the presence of small amount of moisture, then the curve still stable till 430°C temperature of Polystyrene degradation.

From figure 11: first weight loss at 50 °C probably due to humidity and the second deep weight loss at 150 °C due to decompose of some minerals salts (calcium sulphate) then the curve is stable.

TGA curve of semi-arid soil: first weight loss at 60°C due to water loss then small weight losses at 410 °C and 470 °C, the TGA decomposition

**Differential Scanning calorimetry DSC**

Thermal degradation was studied by differential scanning calorimetry under nitrogen flow. Cellulose shows one big endothermic curve at 80°C; from the curve the Cellulose decomposition higher then 200 °C.

In the DSC curve of PAM we can identify a glass transition in the range of 58.05-62.39 °C, a big endothermic Peak at 120°C. For Polystyrene DSC curve is more stable at high temperatures.

DSC curves of semi-arid soil with (PAM + Cellulose) show a pig peak concentrated at 60-80 °C indicated the presence of Cellulose then the curve is more stable.

### Table 3: Physical and chemical properties of Semiarid soils (0-20cm)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>(C + Si)</th>
<th>CO.S</th>
<th>f.S</th>
<th>CO.Si</th>
<th>MO</th>
<th>CaCO₃</th>
<th>EC (mS/cm)</th>
<th>CEC (meq /100g Soil)</th>
<th>PH</th>
<th>Soil textural</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>36.18</td>
<td>19.72</td>
<td>24.34</td>
<td>13.61</td>
<td>6.15</td>
<td>3.2</td>
<td>15.94</td>
<td>0.52</td>
<td>30.8</td>
<td>7.24</td>
<td>Clay</td>
</tr>
</tbody>
</table>
For DSC curves of arid soil with (PAM + Cellulose) we can see two endothermic peaks, the first at 155°C and the second at 170°C.

**X-ray analysis**

XRD analysis showed that Cellulose in the case of PAM (Polyacrylamide) the crystalline peaks appear in the range 21° - 42°.

In case of Polystyrene a crystalline peak appear at 19.65°, for Cellulose Alfa-Alfa a crystalline peak appear at 22.47°, but for casting Polyacrylamide it’s amorphous.

**Thickness of sub layer film**

The thickness of sub layer obtained was from 0.2-0.8 mm.

**Soil water retention**

In this experiment water application was controlled and no percolation losses occurred through the container, therefore any other factor that affected water accumulation was thought its effect.

From Table 3 and Table 4, the amount of water retained by semi arid soil and arid soil increased by adding small amount (0.03%-1%) of polymer and biopolymer to the soil.

The water retention in semi-arid soil treated with polymers and biopolymers showed better growth than in control or with only polymer or only biopolymer. NB: All the treatments had three replicates.

**CONCLUSION**

Different polymer and biopolymer were tested for their efficacy to retain water, augment water holding capacity, and reduce water losses by evaporation and deep percolation.

These synthetic and natural polymers show possible applicability as blend and composite on agriculture especially at desert regions to improve physical properties of soils by binding particles together and retain water.

Among prepared composites and blend polymers, the Polyacrylamide-cellulose blend showed positive results concerning water retention and improving soil proprieties.

Polyacrylamide-Cellulose mixture at arid and semi-arid soils can increase the retention of water against evaporation losses, also the synthetic Polystyrene sub layer act as a barrier to avoid water losses by deep percolation.

The water retained by polymers can be used by the plants and this addition enhanced plant growth and improved water use efficiency.

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REFERENCES


