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Optimization of Nano Graphite Oxide and Others for Super Absorbent Nano Composites Polymeric Materials

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Abstract: Synthesize Super Absorbent Polymer Nano Composites (SAPNCs) is done by addition of three nano materials individually to the neat blend which formed from carboxymethyl cellulose, starch and alum as cross-linker. These materials are nano Graphite Oxide (GO) Silica Nano Particles (SNP) and nano Hydroxy Apatite (HA). SAPNC with nano GO showed higher absorption capacity (69 g) than those prepared from SNP (64 g) and from HA (59 g), therefore, several samples of SAPNC were prepared with 0.1, 0.2, 0.3, 0.4 and 0.5 wt.% nano GO. Many tests suggest that GO with the neat blend forming a structure similar to the molecular sieves with an entrance which enhance water molecules to enter to the new structure which is responsible for the above increment beside the hydrogen bonding formation. As the GO concentration increased and reached the maximum absorbency at 0.3%. After that the absorbency decrease. This is due to the excess GO which partially or completely plug the entrance of structure. Sodium chloride effect on the swelling behaviors of GO-SAPNA was studied and showed absorption reduction with the increasing of the ionic strength of surrounding media. Results showed that SAPNC with 0.3 wt.% nano GO have highest free swelling ratio, highest Absorbency Under Load (AUL) and lowest re-swelling ability while SAPNC with 0.5 wt.% of nano GO have the opposite corresponded values.

Key words: Superabsorbent polymer nano composites, absorption capacity, Nano graphite oxide, molecular sieves, sodium chloride, lowest re-swelling

INTRODUCTION

Super Absorbent Polymers (SAPs) represent special polymeric materials which can appear in a gel state as a result of absorbing huge amounts of water and aqueous solutions (Wang *et al*., 2009). SAPs can absorb deionized water up to 1000 g/g while an absorption capacity for the ordinary hydrogels is not exceeds 1g. This ultrahigh absorption capacity makes SAPs ideal for many absorbing applications like disposable diapers, holding soil moisture, adults incontinence pads, medicine for drug delivery systems, bandages to absorb surgical fluids and controlled release medium (Elliot, 2010). Furthermore, these high water contents give the resultant hydrogels a flexibility level comparable to that of the natural tissue.

SAPs, consist generally from polymeric chains network which are cross-linked to overcome the dissolution tendency and to support water diffusion into the network (Assmann, 2013).

Super Absorbent Polymer Composites (SAPCs) as well as Super Absorbent Polymer Nano Composites (SAPNCs) were manufactured from the addition of several clay (kaolin, diatomite, mica, bentonite, etc.,) or nano sized materials such as silver or gold by the solution or inverse suspension polymerization (Wang *et al*., 2009).

The mechanism of the swelling process contains the following actions: solvent molecules penetrate the polymeric networks structures. Simultaneously, the molecular chains among the cross-linked points expanding therefore are reducing their enthalpy values. This new molecular network structure has an elastic contractive force which increases the contraction tendencies of the networks (Mathur *et al*., 1996).

Unless these two opposed forces get their balance state, expansion and contraction tendencies cannot reach their equilibrium also. So, the osmotic pressure will be the driving force behind the swelling expansion while the elastic force within the network is responsible of the gel contraction (Gao, 2002).

MATERIALS AND METHODS

In order to synthesize SAPNCs based on the prepared CMC/starch blend (Braihi *et al*., 2014) three nano

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materials were added individually. These additives are nano Graphite Oxide (GO) with 3-4 nm thickness, Silica Nano Prticles (SNPs) with 25-43 nm and nano hydroxyapatite (<100 nm). The prepared CMC/starch blend with 1875 g/mol molecular weight and consists of 41.635, 4.875, 48.978 and 4.512 wt.% of carbon, hydrogen, oxygen and aluminum respectively. The particle size of the used CMC/starch blend is 100-120 μ. Nano graphite oxide was obtained from Alibaba Company (China) while the other two materials were prepared locally in Iraq (Al-Seryawi, 2015; Al-Khafaji, 2014). The sonication mixing technique (for 30 min) was used to insure the good dispersion for these nano additives. Then dried overnight (110°C) and powdered.

Tests: Bag method used to determine the free Water Absorbance Capacity (WAC) and the Absorbance Under Load Method (AUL) used to determine the absorbance capacities under different sodium chloride solution concentrations. WAC recorded over time until maximum swelling degree was reached according to the following Eq. 1:

$$WAC = (W_1 - W_0) / W_0 \quad (1)$$

Where:

W_0 = Dry weight (g)

W_1 = Wet weight (g)

Fourier Transformed Infra-Red (FTIR) used to investigate the absorbing capacity.

RESULTS AND DISCUSSION

Absorption optimization: Figure 1 showed that the addition of nano GO 0.3 wt.% to the prerepared CMC/starch blend which was caused to the highest of absorbance capacity while the addition of nano HA 0.3 wt.% caused to the lowest of the absorbance capacity. SNPs addition caused only slight increasing in the absorbance capacity. These variations in the absorbance capacities are reflection to their structures.

Silica Nano Particles (SNPs) have absorbance capacity l<GO because they contain both hydrophilic and hydrophobic groups on and within their surfaces. This is because SNPs possess different silanol group types, some of these groups attracted with water molecules such as germinal and vicinal groups while siloxane group does not.

Germinal and vicinal groups attracted water molecules via. H-bonding and this hydrogen-bonded water molecules still attracted to silica surfaces up to 170°C under atmospheric pressure. Vicinal groups are positioned

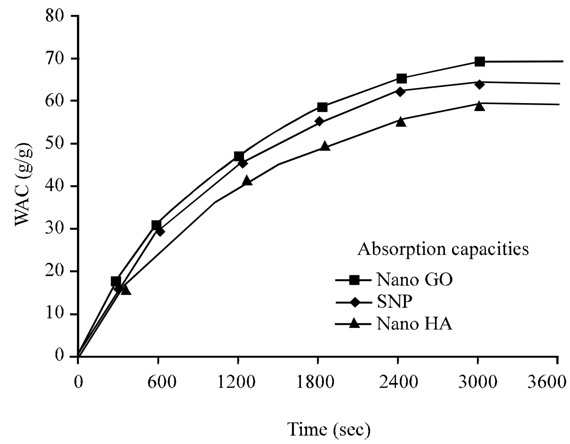

Fig. 1: Nano materials optimization depending on the water absorbance capacity nano GO contains many functional groups which can attracted to water molecules via. inter and intra H-bonding as well as GO particle itself can arises inter H-bonding which can store an additional water amounts

at mutual distances <3 nm, so, they can easily be engaged together by H-bonding from water molecules and form cells to storage water. In contrast isolated silanols groups cannot form these cells because they are located too far apart to be engaged in H-bonding.

Therefore, this variation in the chemical nature of these silanol groups creates an opposite effects on the absorption capacity so decreases it compare with nano GO absorption capacity. Also, SNPs sever from agglomeration tendency which arise from their strong filler filler interactions. This tendency prevent water molecules from penetrate the agglomerated structure. Nano Hydroxy Apatite (HA) shows lowest absorption capacity due to the little amount of hydroxyl groups on its surface.

Swelling behavior kinetics: The swelling ratios of the pure blend and the superabsorbent hydrogels nano composites; SAPNCs (formed by addition different percents of nano GO to the pure blend) were studied. Both WAC and AUL were determined for these hydrogels. The re-swelling behaviors as well as the kinetics of the swelling process were evaluated also.

Water Absorbing Capacities (WAC): From Fig. 2, it was found that the WAC of the neat hydrogel in distilled water was rapid at the first stage and then began to slow down. This rise in rates of swelling in the initial stages is due to the combination of CMC/starch containing polar chains. When the polymeric chains include charges that repel each other, their overall repulsion encourages the swelling by allowing water to penetrate the matrix (Xie *et al*., 2012).

At the final stage it could be seen that the swelling process will stop (the swelling equilibrium could be achieved) within about 50 min. That means that both the expansion (due to solvent penetration via. osmotic pressure) and contraction (due to the decreasing of the

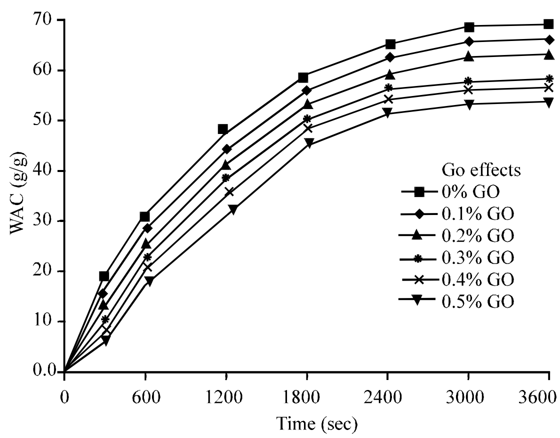

Fig. 2: Water absorbing capacity at different times as a function of nano GO content

configuration enthalpy via. network elastic force) reached the equilibrium state within 50 min under these conditions (Buchholz and Peppas, 1994).

In addition to the above it could be observed that the absorption capacities of SAPNCs hydrogels increased with increasing nano GO content in blend to reach the highest swelling capacity; 69 g in distilled water for SAPNC with 0.3 wt.% GO, versus 58 g for pure blend CMC/starch. These enhancements in the swelling capacities for the SAPNCs including nano GO up to 0.3wt% is due to the plenty of functional groups (such as COOH, -C = O, -OH,-C-O-C-) on the surface of GO particles. These groups enhance the hydrophilic nature of the polymeric structure due to increases their density in the network (Buchholz and Peppas, 1994)

Also, there are strong intermolecular interactions among nano GO particles and the polymer networks which result in holding water, leading to the enhancement of the swelling capacities. However, as the amounts of nano GO content in the polymer blend increased to 0.4% and then to 0.5 wt.%, the absorption tendencies of the SAPNCs reduced. This is because those GO molecules become closer results in interaction between these highly polar molecules, thus, the function of GO reduced and probably plug the way of adsorption water molecules by the gel Fig. 3. This Fig. 3 indicates the decreasing in the

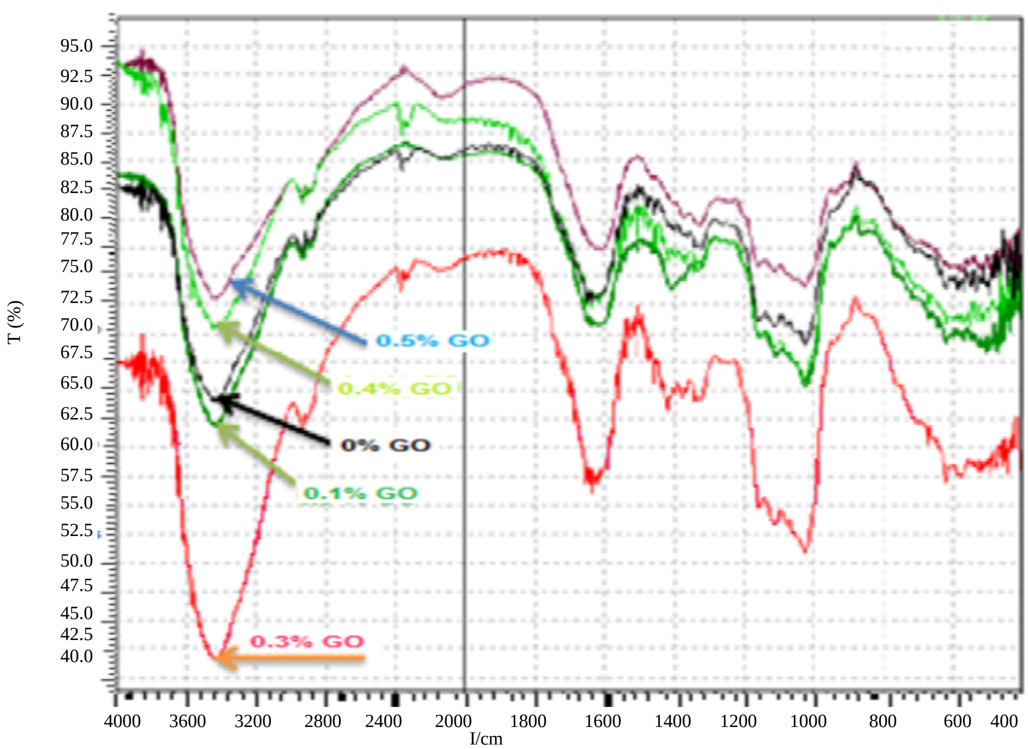

Fig. 3: FTIR spectra for the prepared samples

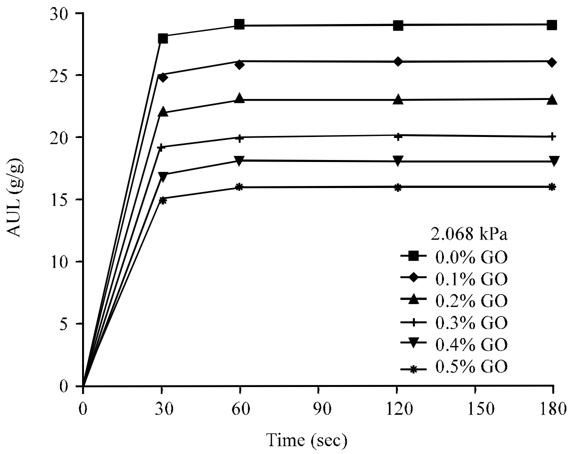

Fig. 4: Time dependence of the AUL for the prepared samples under 2.068 kPa load

intensities of the functional groups (especially, OH group) with the increasing of nano GO content in polymer blend. That means the enhancing of the one-to-one correlation between the number of polar groups and the number of water molecules adsorbed (Elliot, 2010).

Absorbency Under Load (AUL) results: In some SAPs applications, the swelling particles absorb liquids while they were subjected to an external load such as baby weight (hygienic application) and soil weigh in the agricultural application. Therefore, free absorption data are not useful and data for the Absorbency Under the Load applied (AUL) was used by measuring the absorption capacity in (0.9% NaCl) sodium chloride solution under various loads (2.068, 4.136 and 6.205 kPa). AULg can be calculated according to the following equation (Zohuriaan-Mehr and Kabiri, 2008).

$$AUL = (W_2 - W_0)/W_0 \quad (2)$$

where, W_0 and W_2 represent weights of dry and swollen SAP samples under load, respectively.

Figure 4 shows the values of the AUL for the prepared samples under applied load 0f 2.068 kPa (0.3 psi). Samples with 0.1, 0.2 and 0.3% nano GO have AUL values higher than that for sample with 0% GO while samples with ratio 0.4 and 0.5% nano GO have lower AUL values. That means that the stability against shear, the modulus and the swollen gel strength for the gels with nano GO up to 0.3 wt.% were improved compared with the polymer blend free from the free nano GO content. This may be attributed to the new bonding and attractions between the CMC chain and the functional groups on nano GO. On the other hand, the polar interactions in the nano composites containing 0.4-0.5 wt.% ratio of nano GO, causes the AUL values to decrease.

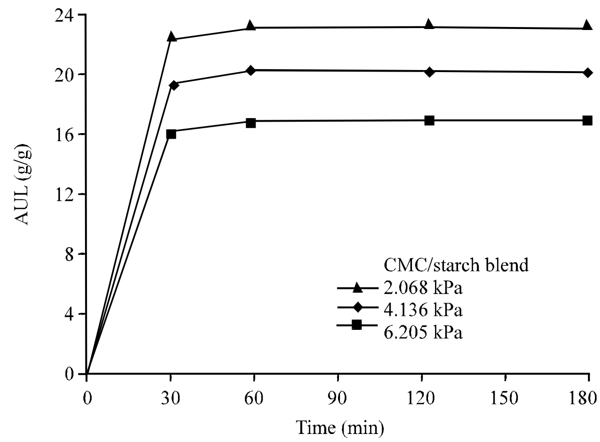

Fig. 5: AUL values for neat blend (under 2.068, 4.136 and 6.205 kPa loads)

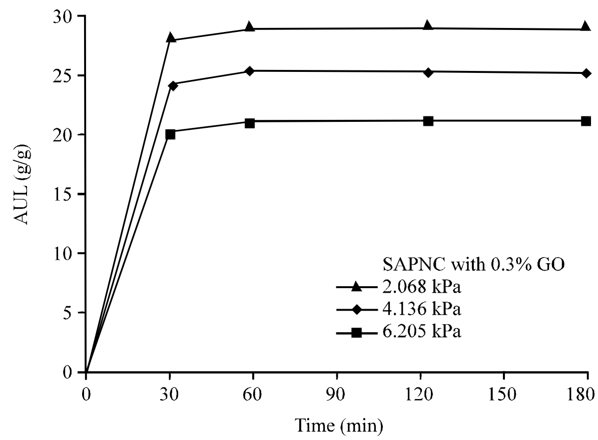

Fig. 6: The AUL for SAPNC with 0.3 wt.% nano GO, (under variable loads)

Figure 5 shows the values of the AUL for the neat blend under various applied loads which are 2.068, 4.136 and 6.205 kPa.

The minimum time needed for the highest AUL value was around 1 h for each load and then all curves will flatten i.e., reach to the level of stability which indicate the independence of the AUL values on the swelling time after 30 min pass of exposure time. Also, it is clear that the AUL values decreases with increase of loading.

As shown in Fig. 6 that the AUL values decrease with increases the values of the applied loads for the SAPNC with 0.3 wt.%. This behavior was similar to the manners that shown in Fig. 5 for the neat blend but with higher values of AUL as compared with those for the neat blend.

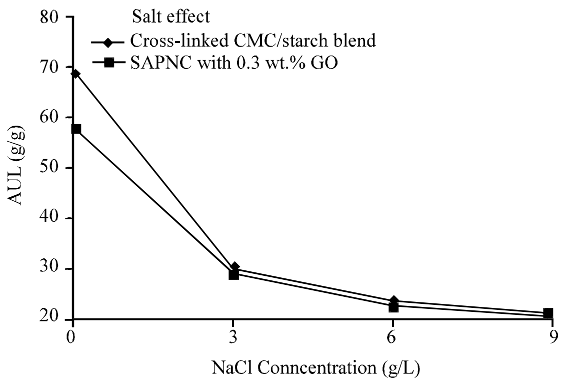

Fig. 7: Swelling curves for CMC/starch blend and SAPNC with 0.3 wt.% nano GO in different NaCl solution concentrations under constant load 2.068 kPa

Sodium chloride salt effect: The effect of NaCl solution on the absorption capacities was measured in NaCl solution with different concentrations (0.3, 0.6 and 0.9%) as shown in Fig. 7.

As shown in this figure, sodium chloride solution absorbency for the superabsorbent decreases with the increasing of the NaCl concentration. This is due to the free chloride ion which has a high penetration power as well as the size of the chloride ion higher than sodium ion, thus, chloride ion destroys the gel structure under load.

This leads to weaken the driving force behind the sodium chloride solution to diffuse into SAP network because of the clear decline of electrostatic repulsion, therefore the sodium chloride solution absorption decreased (Elliot, 2010). These results agree with the Flory's swelling theory. According to this theory, the difference of the osmotic pressure between SAP network and NaCl solution decreased with increasing of the NaCl concentration.

CONCLUSION

Optimization of nano materials showed that nano graphite oxide has higher absorption capacity (69 g water/g sample) as compared to the nano silica and nano hydroxyapatite as well as the prepared CMC/starch hydrogel polymer blends. SAPNCs with nano graphite oxide form a network with entrance likes molecular sieve network. As the GO concentration increased more than 0.3 wt.%, both free and under load absorbencies decreased while the re-swelling ability increased which indicates that the concentration of GO is critical for absorbency tendency.

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