Modification of Chitosan as Chemical Admixture for Cement Pastes

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THREE different composition ratios of chitosan-g-acrylic acid, P[Ch-g-AA] were prepared in the presence of potassium persulphate as an initiator using free radical technique. The grafted copolymers were characterized through FT-IR, TGA, DSC, and SEM. The results showed that these grafted copolymers have a single glass transition indicating that these copolymers can form a miscible phase. The P[Ch-g-AA] exhibit thermal stability. SEM of the grafted copolymers showed no phase separation, when compared with the pure Ch. The effect of grafted copolymers on the physico-mechanical properties of cement pastes was investigated. The addition of water mixed with grafted copolymer to the cement, improves properties of cement pastes. As the ratios of AA in the grafted copolymer increases, the water-to-cement (WC) ratio, setting time as well as water absorption decreases. While The compressive strength was sharply increased at nearly all hydration ages.

Keywords: Chitosan, Acrylic acid, Grafting polymerization, Portland Cement

Introduction

Polymer based admixtures are added to the concrete containing water, aggregates and cement to improve the properties of concrete including workability, chemically combined and compressive strength [1-5]. There are four kinds of polymeric based admixtures including polymer lattices, powder, water-soluble and liquid polymer, the properties and applications of polymer modified mortar and concrete were investigated [6]. The effect of poly [carboxylate-g-(ethylene glycol) methylether] P (C-g-E) on the dispersibility in cement paste are strongly affected by reaction temperature and reaction time of grafting polymerization [7]. Negim at el., [8] investigated the effects of polyvinyl acetate-g-polyoxyethylene monomethylether (MPOE-g-PVAc), and Methoxypolyoxyethylene-g-poly maleic anhydride [9] on physico-mechanical properties of cement. The addition of graft copolymer to cement improve the properties of cement pastes. However, increasing the quantity of the grafted copolymer leads to decreasing of the water-to-cement ratio and setting time also decreases. The effect of the methacrylic ester based polycarboxylate chemical admixture possessing hydroxy terminated poly (ethylene glycol) side chains in cement was tested by measuring paste flow, adsorption and the copolymers possessing side chains of 45 ethylene oxide units was evaluated by heat calorimetry [10]. The macromonomers based on hydroxy terminated poly (ethylene glycol) methacrylic ester chemistry allow to produce chemi-
cal admixture of high workability [10]. Yulia and Tmara [11] studied the composition of cement with the chitosan additive and the results have shown that the addition of chitosan did not reduce the strength of the cement and the optimum amount of chitosan was in the range of 0.6 to 1% of cement mass. Lasheras et al., [12] reported that chitosans of different molecular weights were used as cement admixture to improve the rheological properties of cement pastes because of its capability complexation with heavy metals. The highest molecular weight chitosan showed the greatest effectiveness complexations with heavy metal. Authors modified chitosan superplasticizer by amidation and sulfonation through reaction with maleic anhydride using sodium metabisulfite as an initiator. The results showed the modified chitosan has high water-reducing ratio, fluidity and compressive strength at low water/cement ratio [13].

In this paper, modification of chitosan by grafting polymerization with acrylic acid (AA) and the effect of grafted copolymer on the properties of cement pastes were investigated.

**Experimental**

**Materials**

Chitosan (88 % deacetylation) (Ch) was purchased from R & M Marketing supplied, UK. Acrylic acid (AA), glacial acetic acid, potassium persulphate 98 % (KPS), isopropanol alcohol and N, N-dimethylformamide (DMF), barium chloride and sulphuric acid were purchased from Sigma-Aldrich. ALDRICH. All chemicals were used without further purification.

The raw materials used in the present study are Portland cement clinker (PCC) and raw gypsum (G). Each of these raw materials was separately ground in a steel ball mill until the surface area of 3650 and 2800 cm$^2$/g [14] respectively, were achieved. The chemical composition of the raw materials is shown in Table 1. The mineralogical composition of the PCC sample is $\text{C}_3\text{S}$, 58.79 %; $\beta\text{-C}_2\text{S}$, 17.68 %; $\text{C}_3\text{A}$, 8.08 %; $\text{C}_3\text{AF}$, 9.72 %. The ordinary Portland cement was prepared by mixing 96 wt. % PCC and 4 wt. % G in a porcelain ball mill for one hour using 3 balls to assure complete homogeneity of the cement. The Blaine surface area of the cement sample was 3350 cm$^2$/g.

**Synthesis of chitosan derivative**

Graft copolymerization was carried out in a 250 mL three-necked flask equipped with a thermometer, reflux condenser, and stirrer. The following procedure was used for the synthesis of grafting polymers of chitosan (Ch) and acrylic acid (AA) with various ratios of AA, i.e. [M1: (65: 35), M2: (50: 50), M3: (35: 65)]. Chitosan was dissolved in acetic acid (1 %v/v) and stirred continuously at a constant temperature of 65 °C. After the chitosan was fully dissolved, the temperature of the system was strictly maintained at a required value. Freshly prepared potassium persulphate KPS solution about (5 mL) (0.74 mM) was added followed by dropwise addition of AA. The reaction was conducted for two hours with stirring continued at a constant temperature of 65 °C. Then the reaction product was precipitated with isopropanol (250 mL), filtered, washed to remove the unmodified soluble low molecular weight chitosan and dried [15]. It was again subjected to refluxing for 24 h using N, N-dimethylformamide (DMF) about (20 mL) to dissolve and remove the homopolymer. The final grafted polymer was dried under vacuum at 60 °C. The grafting yield (GY %) and grafting efficiency (GE %) was calculated as follows:

**Table 1. The chemical composition of the raw materials, mass %**

<table>
<thead>
<tr>
<th>Oxides Materials</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>SO$_3$</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>L.O.I</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCC</td>
<td>21.48</td>
<td>6.03</td>
<td>4.22</td>
<td>64.29</td>
<td>0.68</td>
<td>0.39</td>
<td>0.21</td>
<td>0.11</td>
<td>2.59</td>
</tr>
<tr>
<td>G</td>
<td>0.58</td>
<td>0.14</td>
<td>0.11</td>
<td>30.08</td>
<td>0.13</td>
<td>45.36</td>
<td>0.07</td>
<td>0.09</td>
<td>23.44</td>
</tr>
</tbody>
</table>

PCC = Portland cement clinker, G = gypsum, L.O.I = Loss on ignition

where 0.99 is the specific volume of the free water. From the following equation [18]:

\[
\xi = 0.99 \times W_e \times dp / (1 + W_t)
\]

Where, 

- \(W_e\) = Weight of evaporable water content 
- \(dp\) = Density of the concrete 
- \(W_t\) = Total water content which is equal to the sum of evaporable water \((W_e)\) and combined water \((W_n)\) contents.

## Results and Discussion

Based on the calculations, the grafting yield \((GY)\) up to 80.1% and grafting efficiency \((GE)\) of 59.82% were achieved. According to this, chitosan was successfully grafted to acrylic acid.

### IR spectroscopy spectrum

The IR spectra of the chitosan and the grafted chitosan with acrylic acid are shown in Figure 1. Figure 1(a) showed that the main characteristic peaks of chitosan are at 3436 cm\(^{-1}\) (O–H stretch), 2922 cm\(^{-1}\) (C–H stretch), 1635 cm\(^{-1}\) (N–H bend), 1384 cm\(^{-1}\) (C–N stretch) and 1111 cm\(^{-1}\) (asymmetric stretching of the C–O–C bridge). For the spectrum of grafted chitosan, in Figure 1(b), some new absorption peaks appeared. The peak at 1565 cm\(^{-1}\) corresponds to the C=O vibrations of acrylic acid introduced onto the chitosan. The shift of the carbonyl absorption band to lower frequencies could be due to grafting of acrylic acid on chitosan. The peaks at 1219 cm\(^{-1}\) and 1264 cm\(^{-1}\) corresponded to the C-O stretch of the acid. At 3059 cm\(^{-1}\), 2687 cm\(^{-1}\) and 2609 cm\(^{-1}\) attributed to OH stretch of the acid. The peaks at 1459 cm\(^{-1}\) and 1433 cm\(^{-1}\) indicated the OH bend of the acid. Another new band attributed to amines is observed in the region 890-521 cm\(^{-1}\). This strong, broad band is due to N–H wag and observed only for secondary amines. The C–N stretching vibration of amines is observed as medium or weak bands in the region 1150-1066 cm\(^{-1}\).

### Differential Scanning Calorimetry (DSC)

Glass transition temperatures \((T_g)\) for pure Ch and P[Ch-g-AA] with different composition were calculated from the corresponding typical DSC traces as given in Figure 2a-d and Table 2. From Figure 2a-d, it can be seen, there is only one \(T_g\) in the DSC curves due to the miscibility of grafting copolymers. The \(T_g\) value for pure Ch is 92.92 °C as shown in Figure 2a. From Figure 2b-d, it can be seen that \(T_g\) of grafted copolymers moves towards the higher \(T_g\) with increasing AA ratio than pure. The increasing in \(T_g\) is due to the degradation of cross-linked structure. Grafted copolymer with 35% AA (M1) gave the lowest \(T_g\) with 77.23 °C as shown in Figure 2b, while grafted copolymer with 65% AA (M3) gave the highest \(T_g\) with 104.34 °C.

### Thermogravimetric analysis (TGA)

TGA is considered as the most important method for studying the thermal stability of grafted copolymer [19]. The thermal behaviour of pure Ch and P[Ch-g-AA] was evaluated with TGA, DTG in air at a heating rate of 10°C/min and DSC at the same heating rate under nitrogen atmosphere. The TGA thermogram for the pure Ch and grafted copolymers are given in Figure 3a-d.

Table 2 summarize the TGA results of the pure Ch and grafted copolymers with different feed of AA. Two significant weight loss stages are observed in the TGA curve of pure Ch (Figure 3a). The first weight loss (about 12.7%) at 30-202.36°C may be due to loss of moisture and thermo-chemical decomposition of the chemically active organic materials at this range. The second weight loss (about 55.6 %) at 202.36-897.27 °C is attributed to the thermal degradation of CH, as previously reported by several authors [19].

On the other hand, the thermal behavior of grafted copolymers proceeds in 3 stages. It is suggested that the intermolecular hydrogen bonds between the two components do not affect the process of anhydride formation, which corresponds to water loss and crosslinking, as the same result was obtained by authors [20]. The first weight loss (about 35.2%) occurs at 29.7 and 314.6 °C for M1 (Figure 3b), (about 32.5%) occurs at 29.7-287.32.85 °C for M2 (Figure 3c) and (about 17.5 %) occurs at 29.49 – 198.7 °C for M3 (Figure 3d) respectively, which is related to the evaporation of residual moisture and solvents.

The second weight loss occurs at 314.6-462.02...
Fig. 2. DSC thermograms of (a) pure Ch, grafted copolymer: (b) M1, (c) M2 and (d) M3.

198.7 °C for M1, at 287.32-593.2 °C for M2 and at 198.7-366.2 °C for M3. These weight losses could be attributed to the exothermic decomposition of the NH₂ group, other part of Ch and residual acetic acid. The third weight loss occurs at 366.2-900.9 °C for (M1, 65/35) and at 593.2-899.2 °C for (M2, 50/50), and 462.02-900.3 °C for (M3, 35/65) which corresponds to the side chain decomposition of Ch and the main chain of the AA molecule due to broken inter- and intra-molecular hydrogen bonds between Ch and AA.

The weight loss of degradation depends upon many factors such as the surrounding atmosphere, temperature, kinds and composition of the polymer [21, 22]. For example, in the range between 198.7 and 366.2 °C, grafted copolymer with ratio (M3, 35/65) showed more thermal stability (lower weight loss) than (M2, 50/50), (M1, 65/35) and pure Ch respectively.

The maximum initial decomposition temperature (IDT_max) corresponds to the temperature at which the initial degradation may occur [23]. It was observed that IDT_max of pure Ch and grafted copolymer with ratio 35/65 (M3, Figure 3c) is higher than 300 °C, which is above the highest rheological measurements employed in this study and decomposition temperature as shown in the Table 2. While the IDT of grafted copolymer with ratios 50/50 (M2, Figure 3c) and 65/35 (M1, Figure 3b) is 230 °C.

The IDT_max of the grafted copolymer increases as AA ratio in the grafted copolymer increases, which attributed to additional COOH groups of AA and also to the increase in the cross-linking density due to the extension of the network.

Scanning Electron Microscope (SEM)

The scanning electron micrograph SEM of pure chitosan and P[Ch-g-AA] is as shown in Figure 4. The SEM image of chitosan Figure 4a shows a rather smooth surface because there is a stronger interaction between the chitosan molecules. While the SEM image of P[Ch-g-AA] (Figure 4b-d) revealed that uniform distribution of AA might be improving that characteristic nature of chitosan as well as AA. The graft copolymerization of AA modified the surface morphology of chitosan [24]. It can be seen from Figure 4b-d the films of grafted copolymers have homogeneous
TABLE 2. Thermal properties of Ch and P[Ch-g-AA] films.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Step stage</th>
<th>Temperature range (°C)</th>
<th>Weight loss %</th>
<th>Residue %</th>
<th>IDT$_{\text{max}}$ b, °C</th>
<th>$T^*_c$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ch</td>
<td>1</td>
<td>29.4-202.4</td>
<td>12.7</td>
<td>87.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>202.4-897.3</td>
<td>55.6</td>
<td>31.7</td>
<td>310</td>
<td>92.92</td>
</tr>
<tr>
<td>Ch-g-AA (35/65)</td>
<td>1</td>
<td>29.7-314.6</td>
<td>35.1</td>
<td>65.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>314.6-462.1</td>
<td>17.3</td>
<td>47.7</td>
<td>230</td>
<td>77.23</td>
</tr>
<tr>
<td>M1</td>
<td>3</td>
<td>462.1-900.3</td>
<td>16.1</td>
<td>31.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ch-g-AA (50/50)</td>
<td>1</td>
<td>29.7-287.3</td>
<td>32.5</td>
<td>67.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>287.3-593.2</td>
<td>35.1</td>
<td>32.5</td>
<td>230</td>
<td>93.91</td>
</tr>
<tr>
<td>M2</td>
<td>3</td>
<td>593.2-899.2</td>
<td>8.7</td>
<td>23.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ch-g-AA (65/35)</td>
<td>1</td>
<td>29.5-198.7</td>
<td>17.5</td>
<td>82.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>198.7-366.2</td>
<td>59.5</td>
<td>22.9</td>
<td>320</td>
<td>104.3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>366.2-900.9</td>
<td>9.1</td>
<td>13.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Determined from DSC curves.
* Determined from the derivative of TGA

Fig. 3. TGA thermograms of (a) pure Ch, grafted copolymer: (b) M1, (c) M2 and (d) M3
morphology with no domains which confirms the miscibility of the copolymers.

Application of grafted copolymer in cement

Water of consistency (W/C)

Generally, there is directly relationship between the water/cement (W/C) ratio and the quality of concrete produced. The W/C ratio is highly sensitive to the addition of grafting copolymers. Already small amounts of copolymers enhance the workability properties efficiently, but are often associated with strong, undesired retardation phenomena of the setting of the cement paste. The results of water consistency of the various cement pastes mixed with P[Ch-g-AA] are shown in Figure 5. It is clear that the W/C ratio of cement pastes decreases from 0.312 to 0.26 with addition of the grafted copolymer. However, an increase in the AA ratios in grafted copolymer, W/C ratios of the cement pastes decreased. In a general sense, chemical admixtures are often used as water reducers, to make concrete stronger by lowering the water/cement ratio [25].

Setting time

The setting time (initial & final) of pastes studied are given in Figure 6, shows that setting times lengthen with the addition of grafted copolymer to cement pastes. This is mainly attributed to the evaporation of water from the surfaces of the samples mixed with the grafted copolymer is relatively less than that of cement pastes. Furthermore, there may be a relationship between the type of polymers and the setting time of the cement pastes [26, 27]. On the other hand, the setting time of the cement pastes increased with increasing ratios of AA in the prepared grafted copolymers. The delay of setting is thought to relate to the concentration of amide groups in the aqueous phase. The setting time of cement paste depended roughly on the ionic functional group concentration in the aqueous phase of the cement paste [28].

Workability

Figure 7 shows a sharp increase in flow of cement pastes with addition of grafted copolymers. However, an increase in the AA ratios in grafted copolymer latexes, increases the workability of the cement pastes. Mortar mixed grafted copolymer containing 65% (AA) gave the highest flow with 240 mm while cement mixed with grafted copolymer containing 35% (AA) showed a flow measurement of 185 mm. The increase in flow of cement premixed with grafted copolymer due to the surface active of polymer particles improved the fluidity of the concrete [29].

Water absorption

The water absorption of the cement pastes...
Fig. 5. The effect of grafted copolymer on the W/C ratios of cement pastes.

Fig. 6. The effect of grafted copolymer on the setting time of cement pastes.

Fig. 7. The effect of grafted copolymer on the flow of cement pastes.
mixed with grafted copolymers are plotted as a function of curing time as shown in Figure 8. The results of water absorption of the cement pastes mixed with grafted copolymers decreased with the increasing of AA in the copolymer. This is attributed to deposited into the pore structure of the hardened cement pastes as results of the hydration process [30].

**Compressive strength**

The compressive strength of cement mixed with grafted copolymers was shown to increase with the increasing age of curing as represented in Figure 9. The result also showed that the compressive strength of cement mixed with grafted copolymers are higher than that of the pure cement. Furthermore, the compressive strength of the cement pastes premixed with the grafted copolymers solutions increased sharply with increasing ratios of AA in the prepared grafted copolymers. This is attributed to the continuous formation of the hydration products in the pore structure of the hardened cement pastes which increase the process of polymerization [31]. The growth of crystalline structure leads to the strength development and thus, improve the properties of the cement pastes, the higher degree of polymerization between the particles of cement, will lead to higher compressive strength [32-37].

**Conclusions**

Grafted copolymers of acrylic acid (AA) with chitosan (Ch) in three different ratios, of 65:35, 50:50 and 35:65 were prepared and characterized in relation to FT-IR, TGA, DSC, and SEM. From thermal analysis, it is shown that, the degradation profiles of grafted copolymers obtained from aqueous dispersion were influenced by the ratios of AA in the copolymers. The rate of degradation for the P[Ch-g-AA] (35: 65, M3) is the most thermally stable formulation. Transition glass temperature ($T_g$) were determined from DSC. The value of $T_g$ shifted from 92.9 °C to 104.3 °C with increasing the ratio of AA in P[Ch-g-AA]. The SEM’s of Ch and grafted copolymer showed that no phase separation occurs, when compared with the pure Ch.

Mixing of cement pastes was premixed with the grafted copolymers improves the properties of the cement pastes. The W/ C-ratio decreases and setting times (initial and final) were prolonged, that is, especially with the 30% and 50% AA in the grafted copolymers. Flow of cement mixed with grafted copolymers is higher than that of cement pastes without polymer, due to the fact that a large quantity of air is entrained in cement because of an action of the polymer contained in cement. Cement premixed with grafted copolymer containing 60% AA exhibited lower water absorption than that of another content of AA in copolymers and reference cement (M0), while compressive strength increased sharply compared with those of reference cement pastes (M0). As the ratio of AA
in the grafted copolymer increased, the compressive strength of the cement pastes also increased. The grafted copolymer of AA with chitosan act as a rheology modifier when mixed with the cement pastes.

Acknowledgments

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**Fig. 9. The effect of grafted copolymer on the compressive strength of cement pastes**


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