Bull. Mater. Sci., Vol. 37, No. 3, May 2014, pp. 603–608. © Indian Academy of Sciences.

Characterization of gamma irradiated plasticized carboxymethyl cellulose (CMC)/gum arabic (GA) polymer blends as absorbents for dyestuffs

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MS received 18 January 2013; revised 27 March 2013

Abstract. Polymer blends based on carboxymethylcellulose (CMC) and gum arabic (GA) were prepared by solution casting method. Glycerol was added to the polymer blend solution as a plasticizer with different ratios (2·5, 5, 10 and 20%). Then, the plasticized blends were exposed to gamma irradiation at different doses (5, 10 and 20 kGy). The physical properties of the plasticized polymer blends were investigated in terms of gel fraction (%) and swelling percent (%). Thermal properties were investigated by TGA. Also, the structure of the plasticized polymer blends was characterized by Fourier transform infrared spectroscopy. Scanning electron microscope was investigated in order to examine the compatibility between two polymers in the blend and also between polymer blend and plasticizer. The prepared plasticized polymer blends were used as an adsorbent for different dyestuffs. The sorption of dyestuffs by the plasticized polymer blend was determined by a method based on spectroscopic analysis. The results showed that the plasticized polymer blend has a high affinity for basic, acid, reactive and direct dyes. The obtained results showed that using glycerol as plasticizer improved the swellability of polymer blend and also the dye uptake (%).

Keywords. CMC; GA; plasticizer; gamma radiation.

1. Introduction

Recent research and development of polymer materials have been directed to blending of different polymers to obtain new products having some of the desired properties of each component. Natural polymers are easily degradable and plentiful in resource and used widely in many industrial fields (Jianfa *et al* 2009).

Sorption by material of biological origin appears to offer a technically feasible and cost-effective approach to solve the problem of pollution (Volesky 2001).

Adsorbents, derived from natural polymers, such as cellulose, chitin, chitosan and their derivative have been identified as an attractive option because of their economic efficiency, distinctive properties, safety and biodegradability (Majeti and Kumar 2000; Isogai 2001). Carboxymethyl cellulose (CMC), the most popular and cheapest cellulose ether is well known as a safe and biodegradable material, which is widely used as food additives, washes, paste, etc. It is an anionic and water-soluble natural polymer derivative. It is widely used in detergents, oil exploration, food applications, paper and textile industries due to its high viscosity (Guo *et al* 1998). The addition of CMC to the cassava starch films increased tensile strength and reduced elongation at break of blended films. This was ascribed to the good interaction between cassava starch and CMC (Mbuna and Mhinizi 2003).

Gum arabic (GA) has been used in different purposes as in food, pharmaceutical, cosmetics and medical purposes (FAO 2000; Wirongrong *et al* 2011). Therefore, the necessity of using safe GA in food processing and medical purposes becomes more important. Ibrahim *et al* (2007) found that polyvinyl alcohol (PVA) polymer can be used as a modifier to improve the physical and mechanical properties of brittle GA polymer. Also, the presence of PVA in higher content protects the GA in the blend from degradation. The optimum ratio of GA in the blend was found to be 20% wt. These blends are very suitable to be used as natural material to release various antimicrobial drugs and also release the heavy metals to improve the agricultural soil.

CMC and GA have abundant hydroxyl groups in their structure hence on blending, hydrogen–bonding interactions between them are expected to occur. As a result, related thermal and mechanical properties could be improved (Ibrahim *et al* 2007).

In the present work, unirradiated and irradiated plasticized CMC/GA blends were prepared by adding glycerol at different concentrations to the blend as plasticizer. Different properties were investigated before and after exposure to various doses of gamma irradiation. The sorption

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capacity of CMC/GA blend for different dyestuffs was investigated.

2. Experimental

2.1 *Materials*

A sodium salt of CMC (pure polymer) in the form of granules, molecular weight (MW) 180,000 was supplied by El-Nasr Pharmaceutical Chemical-Prolabo (Egypt). GA is an exudate from Acacia species tree. GA is considered as heteropolysaccharides which contain more than one type of monosaccharide in complex branched polysaccharides that contains galactose, rhmnose, glucouronic acid and arabinose residues, besides highly branched polymer of various monosaccharides (Anderson and Wang 1990). *N*,*N*′-methylene bisacrylamide (MBAM) from Aldrich, Wisconsin, USA, was used as a cross-linking agent. Glycerol was of pure grade and obtained from (Prolabo, France). Four dyestuffs, belonging to different classes were used throughout this work. These dyes were remacryl blue (basic dye), supplied by Hoechst (Germany); Sandolan E-3GSL (acid dye), drimarene blue K-3GL (reactive dye) and solar orange (direct dye) supplied by Sandoz (Switzerland).

2.2 *Preparation of CMC/GA film*

CMC/GA blends with different compositions (100% CMC, 80% CMC and 60% CMC) were prepared by the solution casting technique. CMC and GA powders were dissolved in distilled water at room temperature. About 0·1 wt% of MBAM as a cross-linking agent was added to the polymer solution. Then glycerol was added to the complete miscible solution as a plasticizer agent with a ratio of (2·5, 5, 10 and 20%). The complete miscible solutions are then casted onto glass dishes to form films with a thickness of ~0·2 mm. The cast films were dried at room temperature for 24 h and then placed in a vacuum oven at 50 °C to remove the residual water.

2.3 *Gamma irradiation*

Irradiation process was carried out using a Co-60 γ cell (made in India) at the National Centre for Radiation Research and Technology, Cairo, Egypt, with a dose rate 6·92 kGy/h. Irradiation was carried out under an air atmosphere. The different polymer blends were exposed to different doses of γ-irradiation (5, 10 and 20 kGy).

2.4 *Characterization of CMC/GA blends*

2.4a *Determination of gel fraction (%)*: A known weight (W_1) of the irradiated blend was extracted by water in a soxhlet apparatus for 24 h and then dried to a constant weight in vacuum (W_2). The soluble fraction (SF) was determined according to the following equation:

$$SF\ (\%) = ((W_1 - W_2)/W_1) \times 100.$$

Thus GF (%) was calculated as follows

$$GF\ (\%) = (1 - SF) \times 100.$$

2.4b *Swelling (%)*: A known dry weight of the insoluble part of the blend (W_1) after calculation of the soluble fraction was immersed in distilled water at room temperature for 24 h. The swollen part of the blend at equilibrium was weighed (W_2).

The swelling percentage (SW) is determined by:

$$SW\ (\%) = (W_2 - W_1/W_1) \times 100,$$

where W_1 and W_2 represent the weight of the dry and wet samples, respectively.

2.4c *FT–IR spectroscopic analysis*: FT–IR spectrophotometer model Mattson 100, made by Unicam (UK) was used for FT–IR measurements over the range 500–4000 cm^{-1}.

2.4d *Thermogravimetric analysis*: TGA studies were carried out using a TGA-30 apparatus (Shimadzu, Kyoto, Japan), at a heating rate of 10 °C/min in air, over a temperature range from room temperature to 600 °C.

2.4e *Scanning electron microscope*: The surface morphology of CMC/GA blend was examined by SEM. The micrographs were taken with JSM-5400 instrument manufactured by Joel, Japan.

2.5 *Dye sorption measurements*

The percentage sorption of the different dyestuffs by CMC/GA was determined by a general procedure based on spectrophotometer analysis. In this regard, standard curves were first constructed, representing a relation between different known concentrations from each dye and the corresponding light absorption (El-Salmawi *et al* 2001). The light absorption of the basic, acid, reactive and direct dyes were measured at wavelengths of 660, 515, 590 and 470 nm, respectively. The different expressions governing these relations were calculated to be as follows:

$$\text{Light absorbance (mg/L)} = 0{\cdot}223 \times \text{basic dye concentration},$$

$$\text{Light absorbance (mg/L)} = 0{\cdot}026 \times \text{acid dye concentration},$$

$$\text{Light absorbance (mg/L)} = 0{\cdot}023 \times \text{reactive dye concentration},$$

$$\text{Light absorbance (mg/L)} = 0{\cdot}046 \times \text{direct dye concentration}.$$

In this procedure, a certain concentration from each dye under investigation (20 mg/L) was first dissolved in certain volume of boiled water solution. A constant weight of plasticized blend (0·5 g) was then immersed in different dye solutions at various lengths of time and then the light absorbance of the residual dye solution was measured. The percentage sorption by the plasticized blend was determined according to the following equation:

Dye sorption (%) = dye concentration on plasticized blend/initial dye concentration × 100.

3. Results and discussion

3.1 *Gel fraction (%)*

The gel fraction (%) of irradiated 100% CMC and GA/CMC polymer blends having different compositions at various irradiation doses was given in figure 1. It can be seen that the increase of GA content in the blend is accompanied with decrease in GF (%) for the same irradiation dose. On the other hand, it can be observed that GF (%) of either 100% CMC or any GA/CMC polymer blend increases with increasing irradiation dose up to 20 kGy due to the occurrence of crosslinking. Moreover, it was found that at a fixed dose 100% CMC posses a high value of gel fraction (%) than the blend. Furthermore, on increasing GA ratio in the blend is accompanied with a decrease in the gel fraction (%) at the same dose. Finally, it can be concluded that there is a marked increase in the gel fraction (%) of irradiated polymer blends especially for blends rich in CMC.

This behaviour was observed on the addition of different concentrations of glycerol (2·5, 5, 10 and 20%) as a plasticizer on 80% CMC/20% GA. The results obtained are shown in figure 2. It can be seen that, the increase of glycerol (%) is accompanied by a decrease in gel fraction for all irradiation doses under investigation. On the other hand, it can be observed that the gel fraction (%) increases with increasing irradiation doses up to 20 kGy for plasticized irradiated 80% CMC/20% GA blend.

3.2 *Swelling (%)*

The swelling parameter is a very important factor for the applicability of the synthetic absorbent. Figure 3 shows effect of glycerol as a plasticizer on the swelling (%) at different irradiation doses (5, 10 and 20 kGy). It is clear that, the swelling (%) increases on increasing glycerol (%) in the blend at different irradiation doses. While increasing irradiation dose up to 20 kGy is accompanied with decrease in swelling (%). Thus, glycerol plays an

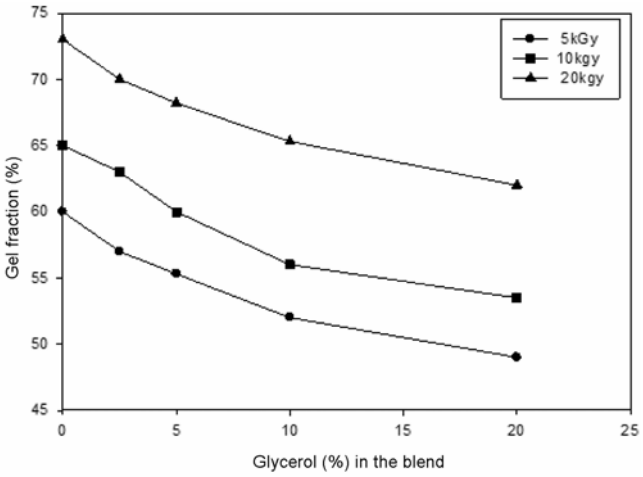

Figure 2. Effect of glycerol concentration in blend on gel fraction (%) at different irradiation doses.

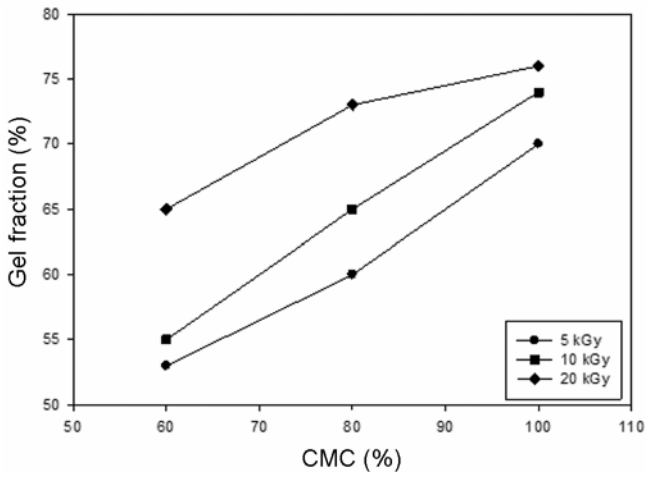

Figure 1. Effect of CMC % in blend on gel fraction % at different irradiation doses.

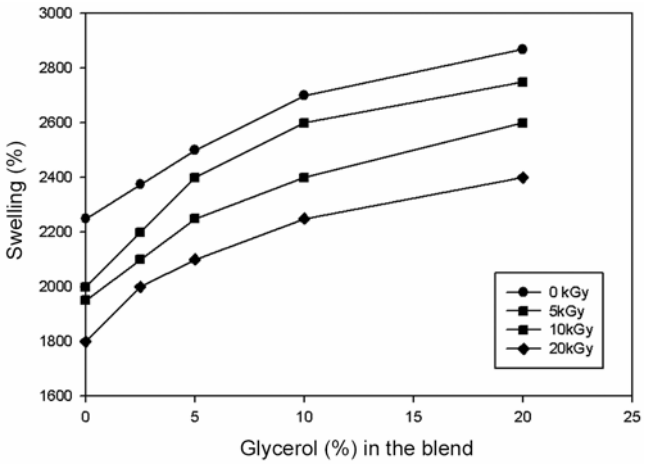

Figure 3. Effect of glycerol (%) in blend on swelling (%) at different irradiation doses.

important role in plasticization of the blend which will be leading to increased swelling (%). Also, the amount of absorbed water by the blend highly depends on irradiation dose. The relationship between water absorption and different irradiation doses was shown also in figure 3. It can be seen that unirradiated blends have the highest swelling (%) values than the irradiated samples. Moreover, the higher the irradiation dose, the lower the swelling (%) this is due to the cross-linking density of CMC/GA increased at higher doses.

3.3 *FT–IR spectroscopic analysis*

FT–IR spectra of plasticized unirradiated and irradiated (20 kGy) 100% CMC and 80% CMC/20% GA blend were shown in figures 4 and 5. In these figures, two strong peaks were observed at 1619 and 1420 cm^{-1} due to the asymmetrical and symmetrical stretching –COO- groups which appeared in unirradiated and irradiated spectra. Characteristic absorption peak of CMC and GA appeared at 3500 cm^{-1} for the hydroxyl groups (Silverstein and Webster 1998; Senna *et al* 2001). In the spectrum of unirradiated spectra there are bands at 2915, 1463 and 719 cm^{-1}, responsible for deformed vibration of CH– groups (Ibrahim *et al* 2006) as shown in these figures. In these figures there was new bands around 1700 cm^{-1} due to C=O absorption characteristic of COOH group of 100% CMC and 80% CMC in the unirradiated and irradiated spectra. However, it seems that polymer blend possesses relatively higher extent of hydrogen bonding than 100% CMC. Generally, slight changes in intensity for most characteristic band after irradiation at 20 kGy was observed. It was found that there is a new and very weak peak appearing at 1·650 cm^{-1} that is attributed to the

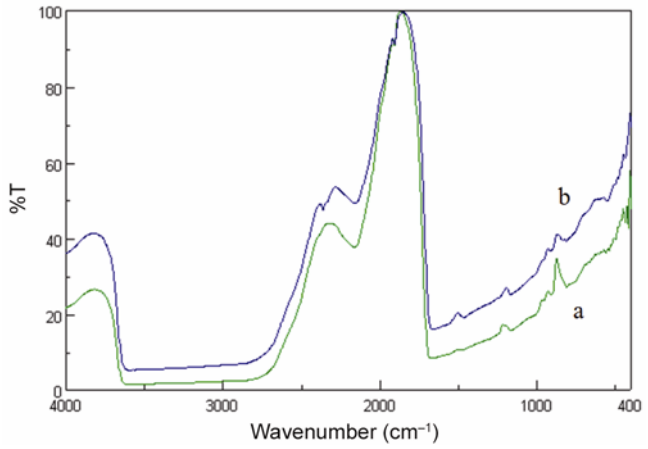

Figure 4. FT–IR spectrum of unirradiated plasticized (a) pure CMC and (b) 80% CMC/20% GA.

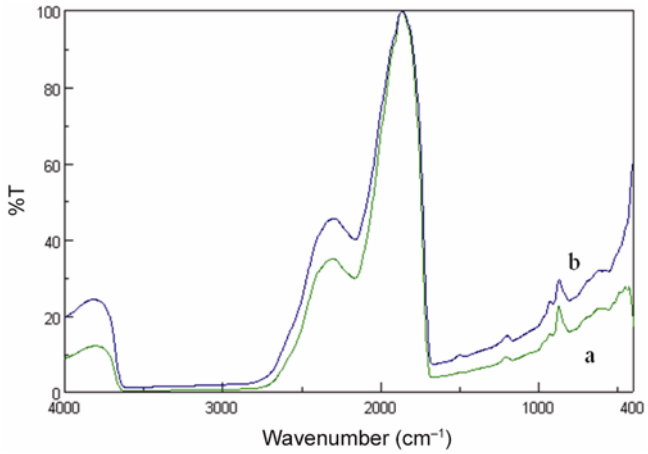

Figure 5. FT–IR spectrum of irradiated plasticized (20 kGy) (a) pure CMC and (b) 80% CMC/20% GA.

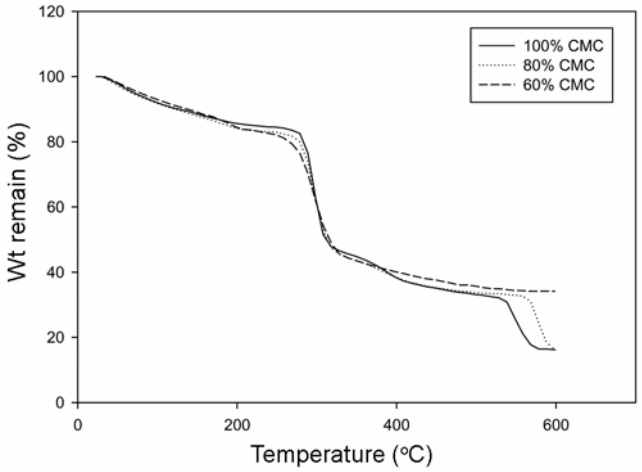

Figure 6. Initial TGA thermograms for thermal decomposition of unirradiated plasticized pure CMC and its blend with different ratios of GA.

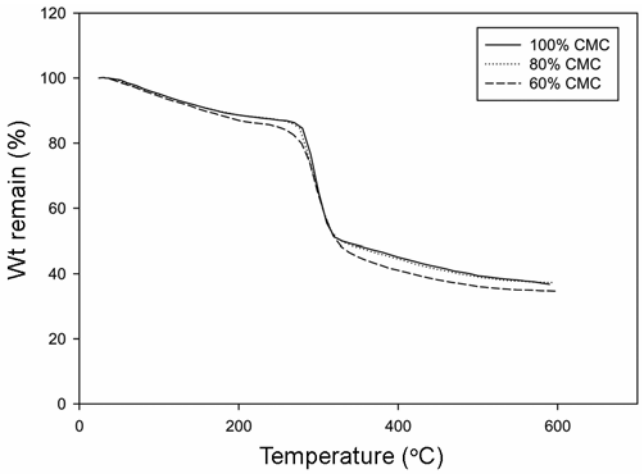

Figure 7. Initial TGA thermograms for thermal decomposition of plasticized irradiated pure CMC and its blend with different ratios of GA at a dose 20 kGy.

presence of amide group of cross-linking agent (MBAM) in the blend.

3.4 *Thermogravimetric analysis*

The thermal stability of plasticized unirradiated and irradiated 100% CMC, 80% CMC and 60% CMC within the temperature range up to 320 °C are shown in figures 6 and 7. From these figures, it was found that there is an increase in thermal stability for irradiated than unirradiated polymer blends as shown in the figures. It is concluded that irradiation increases the thermal stability of both 100% CMC and its blend, which is due to the occurrence of a sort of cross-linking process due to irradiation as reported in another work (Senna *et al* 2001). Figure 8 was deduced from figures 6 and 7 which show dependence of thermal stability on a constant blend composition (80% CMC/ 20% GA), which again confirm the increase of thermal stability on irradiation up to 20 kGy.

3.5 *Morphology by SEM*

Figure 9 shows structural surface morphology of plasticized unirradiated and irradiated 100% CMC and its blend with different ratios of GA. It can be seen that the 100% CMC has smooth and relatively homogeneous appearance. After blending with GA a regular and parallel thin strains at blending ratios of plasticized (80% CMC/20% GA) and (60% CMC/40% GA) as shown in the micrographs (b) and (c). On the other hand, the compatibility has appeared after irradiation at 20 kGy where the molecular chains are compact and oriented parallel to each others as shown in micrographs (d), (e) and (f). The presence of glycerol in the blend is accompanied with an improvement in compatibility.

3.6 *Sorption of dyestuffs by plasticized CMC/GA blend*

There are various types of dyes belonging to different classes depending on the kind of polymer blend to be dyed. For example, the reactive and direct dyes are specific for cotton cellulose fibres, while the acid and basic

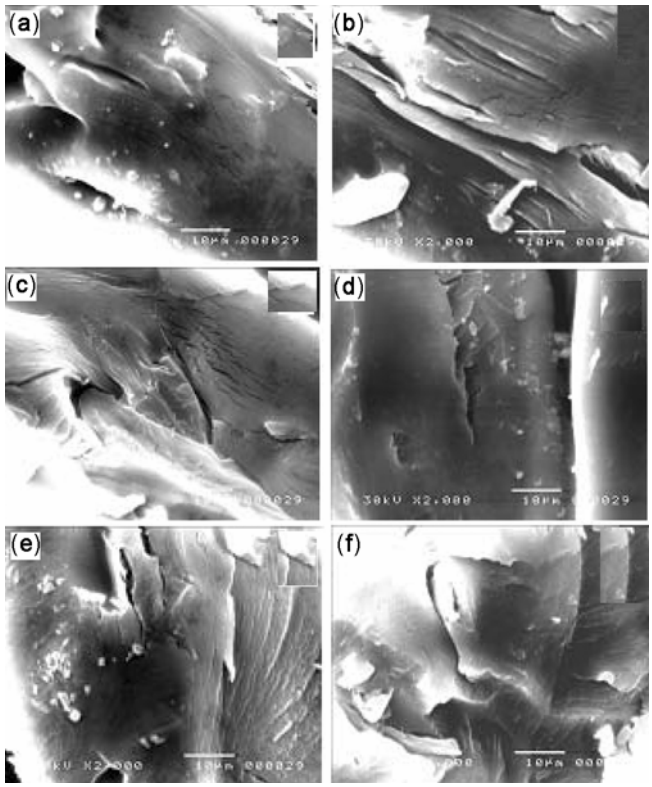

Figure 9. SEM micrographs of different unirradiated and irradiated polymer blends (**a**) unirradiated 100%CMC, (**b**) unirradiated 80% CMC, (**c**) unirradiated 60% CMC, (**d**) 100% CMC (20 kGy), (**e**) 80% CMC (20 kGy) and (**f**) 60% CMC (20 kGy).

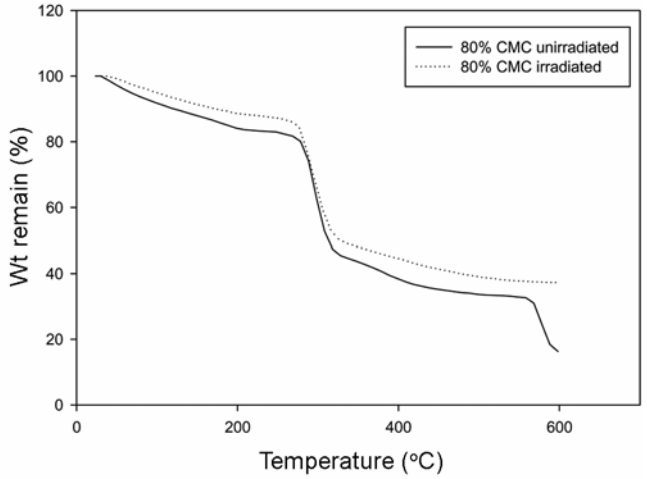

Figure 8. Initial TGA thermograms for thermal decomposition of plasticized 80% CMC/20% GA blend unirradiated and irradiated at 20 kGy.

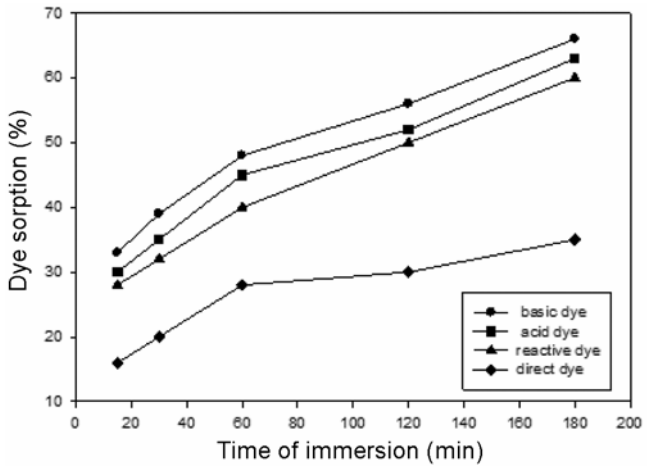

Figure 10. Dye sorption (%) of basic acid, reactive and direct dyes by plasticized 80% CMC/20% GA blend as a function of time.

dyes are used for dyeing protein fibres such as wool and silk. In general, the choice of dyestuffs is based on the functional groups on both fibre and dyestuffs. All these dyes are usually used in textile factories.

In the present work, a solution containing a constant concentration of 20 mg/L of each dye under investigation was prepared. The dye sorption of different dyes by the plasticized 80% CMC/20% GA polymer blends, as a function of the immersion time at room temperature at constant concentration of plasticizer 10% were investigated as shown in figure 10. It can be seen that the dye sorption-time trend by plasticized 80% CMC/20% GA blend differs from one dye to another. In all cases, the dye sorption was found to increase with an increasing time of immersion. The affinity of plasticized blend for the different dyes can be arranged as follows:

Basic dye > acid dye > reactive dye > direct dye.

The affinity of CMC and GA for the different dyestuffs is essentially dependent on the hydrophilic group present in the polymer (hydroxyl group OH^-). Also, the sorption process will eventually go through chemical bonding between the active groups on the different dyes and those of the blend and not through physical absorption. This is because, when the plasticized blend was left in the dye solution for a longer time than 120 min, the adsorption of dyes did not occur. Thus, it may be concluded that dyeing of the plasticized blend with the different dyestuffs is dependent on the relative affinity for each dye. The mechanism of dyeing with basic dyes implies the presence of an anionic part in the medium to react with the cationic part of the dye through an anionic bond. Therefore, the sorption of the basic dye will go through the reaction with the hydroxyl groups of CMC and gum inside the blend.

4. Conclusions

The blending of already existing polymers is of special importance in the field of polymer chemistry. CMC and GA can form a thermodynamically miscible pair. The gel fraction increases with increasing irradiation dose, while swelling of plasticized CMC/GA blend nearly tends to increase with the increasing GA content and reduced with enhanced irradiation doses. Consequently, plasticized CMC/GA blends were selected to be used as an absorbent for dyestuffs.

References

Anderson D M and Wang W P 1990 *Phytochemistry* **29** 1193

El-Salmawi K M, Abu Zaid M M, Ibrahim S M, El-Naggar A M and Zahran A H 2001 *Appl. Polym. Sci.* **82** 136

Food Agriculture organization (FAO) 2000 *Satistical appendix* (Sudan: IMF)

Guo J H, Skinner G W, Horcum W W and Barnum P E 1998 *Pharm. Sci. Technol. Tod.* **16** 254

Ibrahim S M, El-Salmawi K M and El-Naggar A A 2006 *Appl. Polym. Sci.* **102** 3240

Ibrahim M S, Ibrahim S M and Farag S A 2007 *Polym. Plast. Tech. Eng.* **46** 1143

Isogai A 2001 *Material science of cellulose* (Tokyo: University of Tokyo Press)

Jianfa L, Jinhong L and Yimin L 2009 *Appl. Poly. Sci.* **112** 261

Majeti N V and Kumar R 2000 *React. Funct. Polym.* **46** 1

Mbuna J J and Mhinizi G S 2003 *Sci. Fo. Agric.* **83** 142

Senna M M, Aly H A and El-Naggar A M 2001 *Polym. Degrad. Stab.* **71** 53

Silverstein R M and Webster F X 1998 *Spectrometric identification of organic compounds* (New York: Wiley) Vol. 6

Volesky B 2001 *Hydrometallurgy* **59** 203

Wirongrong T, Lisa J M, Sasitorn W, Pensiri S and Pornchai R 2011 *Chem. Cent. J.* **5** 6