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Article

Preparation of Microcrystalline Cellulose from Waste Cotton Fabrics Using Gamma Irradiation

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Abstract. Recycling process of waste cotton fabrics into value added products is still limited. Cotton fabrics are made of cotton fiber, which is a high cellulose source and it can be converted into microcrystalline cellulose (MCC). In this research, MCC was prepared by dissociation of waste cotton fabric using gamma irradiation with various radiation doses in dried phase and in wet phase by 35 % H_2O_2 solution. The properties of the prepared MCC were investigated and compared with standard Avicel PH101 MCC. The results from FTIR spectra and X-ray diffraction patterns show that the obtained MCC has typical similarity to commercial MCC. X-ray diffraction analysis showed that the crystallinity percentage (%Cr) was increased while crystallite size was decreased through gamma irradiation. At the same dose, degree of polymerization (DP) and solubility in water in dried phase, i.e. 135; 5.46 % were higher than wet phase irradiation i.e. 123; 4.38 %. Degree of polymerization and solubility in water decreases with increasing total irradiation dose. The investigated physicochemical properties of the obtained MCC conform to the European Pharmacopoeia requirements. The results indicated that waste cotton fabrics have a great potential as a low cost MCC raw material and can lead to many applications.

Keywords: Microcrystalline cellulose, waste cotton, gamma irradiation, degradation, degree of polymerization

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1. Introduction

An increasing number of textile industries, especially in Indonesia can improve the economy, but will also have a negative impact to the environment such as abundant waste cotton fabrics. Generally, these waste leftover materials of textile industry end in waste stations and are usually landfilled or incinerated which can create environmental pollution. Various processes for waste cotton fabrics recycling have been developed to increase the value-added products such as preparing cellulose derivative [1], composite fillers [2], bio adsorbent [3], and bio energy [4]. Cellulose content in the waste cotton fabrics is very high at around 95 - 99%, so one potential way to high value utilization is to extract them as microcrystalline cellulose (MCC). Due to an excellent compatibility and low chemical reactivity, MCC has been used in the pharmaceutical industry [5], in food applications as a texturizing agent and fat replacer [6], and additive in composite [2].

MCC is a fine, white, odorless, crystalline powder, and a biodegradable material, which is purified, partially depolymerized cellulose prepared by treating alpha cellulose [5, 7]. In industrial manufacture, MCC is obtained from the processing of wood fiber (plant), but in some studies, MCC can be obtained from oil palm biomass residue [7], agriculture residues [8], bacterial cellulose [9], and waste cotton fabrics [2]. MCC is synthesized on an industrial scale by hydrolysis of cellulose using dilute mineral acids. High acids consumption leads to high production cost and environmental problems. Recently there has been a growing interest in various methodologies of MCC production processes to improve its properties. In recent years researchers reported a number MCC synthesis methods such as using thermo catalytic treatment of wood pulp [10], enzymatic hydrolysis of starch [11], ultrasonic and microwave processes of wheat bran [12], and ionizing radiation such as electron beam irradiation of pulp [13] and gamma irradiation of jute fiber [14]. Properties of raw materials and method of preparation influence the overall characteristics of MCC.

Radiation induced cellulose degradation in microcrystalline cellulose preparation is one of the most promising methods because of the easy handling at room temperature, large penetration in cellulose matrix, rapid, scalable, and clean physical process with much less chance of contamination. Generally, high irradiation doses produce free radicals which induce chemical and physical modifications in the cellulose. Interaction of ionizing radiation such as gamma radiation and electron beam radiation with polymer structure consist two simultaneous processes: the crosslinking mechanism, consisting in the creation of new inter or intra chains chemical bonds and the degradation of polymer structure. Synthesis and characterization of MCC from waste cotton fabrics have previously been reported, but until now no researchers have reported a comprehensive synthesis and characterization of MCC from gamma irradiation of cotton fabrics, or its comparison with commercial MCC. In the present study, the synthesis and characterization of MCC from waste cotton fabrics using simultaneous gamma irradiation technique were studied. The chemical structure and crystallinity of MCC were investigated to confirm and to monitor the structural changes induced by gamma irradiation. The effects of medium phase and irradiation doses on MCC characterization were investigated and discussed in detail.

2. Experimental Procedure

2.1. Preparation of Microcrystalline Cellulose using Gamma Irradiation

Waste cotton fabrics were collected from tailoring workshops and subjected to cutting and shredding processes. MCC was prepared by disintegrated waste cotton using 35 % hydrogen peroxide for 2 hours at 90 ^{0}C. The mixtures were irradiated using Gamma Chamber-40 with varying total dose of 10, 30, 50, 70, and 100 kGy at the dose rate of 10 kGy/hr. Irradiations were accomplished in open atmosphere and at room temperature. MCC was washed with distilled water and grounded into a fine powder by using rotary ball mill.

2.2. Characterization of Microcrystalline Cellulose

Characterization using FTIR spectroscopic technique of sample was carried out to follow the change in the functionality of cellulose as a result of gamma irradiation. FTIR study of MCC was done using Thermo Nicolet Avatar FTIR spectrophotometer. X-ray diffraction studies were performed under ambient

conditions, using X-ray Diffractometer XRD (Shimadzu tipe 6000). Percentage crystallinity (%Cr) [15] was calculated according to Eq. (1).

$$\%Cr = \frac{I_{22}}{I_{22} + I_{18}} \quad (1)$$

Where, I_{22} and I_{18} are the crystalline and amorphous intensities at 2θ scale close to 22^0 and 18^0, respectively. Crystallite sizes were calculated from the Scherrer equation [16] as follows:

$$L = \frac{k\,\lambda}{\beta \cos\theta} \quad (2)$$

where L is the size of crystallite (nm), k is the Scherrer constant (0.94), λ is the X-ray wavelength (0.15418 nm), β is the FWHM (full width at half maximum) of the lattice plane reflection in radian, and θ is the corresponding Bragg angle (reflection angle).

Degree of polymerization (DP) of cellulose samples was determined by viscosity measurements in a cupri ethylenediamine solution using an Ostwald viscometer according to European Pharmacopoeia [10] standard and then calculated using Eq. (3).

$$DP = \frac{95 \times \eta_c}{m \times \left(\frac{(100 - b)}{100} \right)} \quad (3)$$

Where, m is the material mass and b is the loss on drying (%). Solubility in water of MCC and physicochemical properties were carried out in accordance with European Pharmacopoeia [17].

3. Result and Discussion

3.1. Characterization of Microcrystalline Cellulose Using FTIR Spectroscopy

FTIR spectroscopy was employed to confirm the successful synthesis of MCC by comparing functionality of the original cellulose with that of MCC product and MCC commercial. Figure 1 show FTIR spectra of original cellulose from waste cotton fabrics, MCC that was prepared by using the different radiation doses at wet phase irradiation, and MCC commercial. All spectra results revealed almost similar spectra patterns to commercial MCC which is an indication that synthesized samples have similar characteristics and chemical composition to commercial MCC. The presence of OH stretching and C-H stretching vibration is indicated by the broad absorption band at around 3300 cm^{-1} and 2900 cm^{-1} [16, 17]. The broad absorption band around 1650 cm^{-1} is due to C=O stretching, and the absorption around 1064 cm^{-1} is related to C-O-C glycosidic. The most obvious characteristic of the cellulose spectra is the presence of the absorption band at 894 cm^{-1}, which indicates C-H vibration characteristic of β-glycosidic linkages between the anhydroglucose units in cellulose [18]. These similar results were observed in isolating MCC from waste cotton fabrics using mixed acid hydrolysis [2]. Another study also obtained similar FTIR spectra while preparing MCC from Alfa fibers [16] and fruit waste [17] using acid hydrolysis. No significant effect on FTIR spectra was observed for gamma irradiation dose ranging from 0 to 70 kGy which indicates no strong reaction occurred. At irradiation dose of 100 kGy, FTIR spectra were observed differently in the peak intensity. Broad absorption of OH and C-H stretching decreases due to condensation reactions which is a decrease of intermolecular hydrogen bonds. This result showed a good agreement with Danu et al. [19] upon degradation of oil palm empty fruit bunch by electron beam irradiation. The absorbance of carbonyl groups at 1650 cm^{-1} and asymmetric C-H deformation in hemicelluloses at 1460 cm^{-1} decrease until almost disappear completely. Baccaro et al [20] obtained a similar result for gamma irradiated pure cellulose. Disappearance of the absorbance of irradiated maple wood cellulose by CO_2 laser was also evident [21]. Condensation reactions of lignin and deacetylation of hemicelluloses as a consequence of the oxidative degradation due to higher irradiation doses may eliminate the absorbance. The decrease in the broad absorption at 1064 cm^{-1} and 894 cm^{-1} is caused by cleavage of β-glycosidic linkages. At high irradiation dosages, the cleavage reactions were duplicated and resulted in an increase of glycosidic bonds breakage [20, 22].

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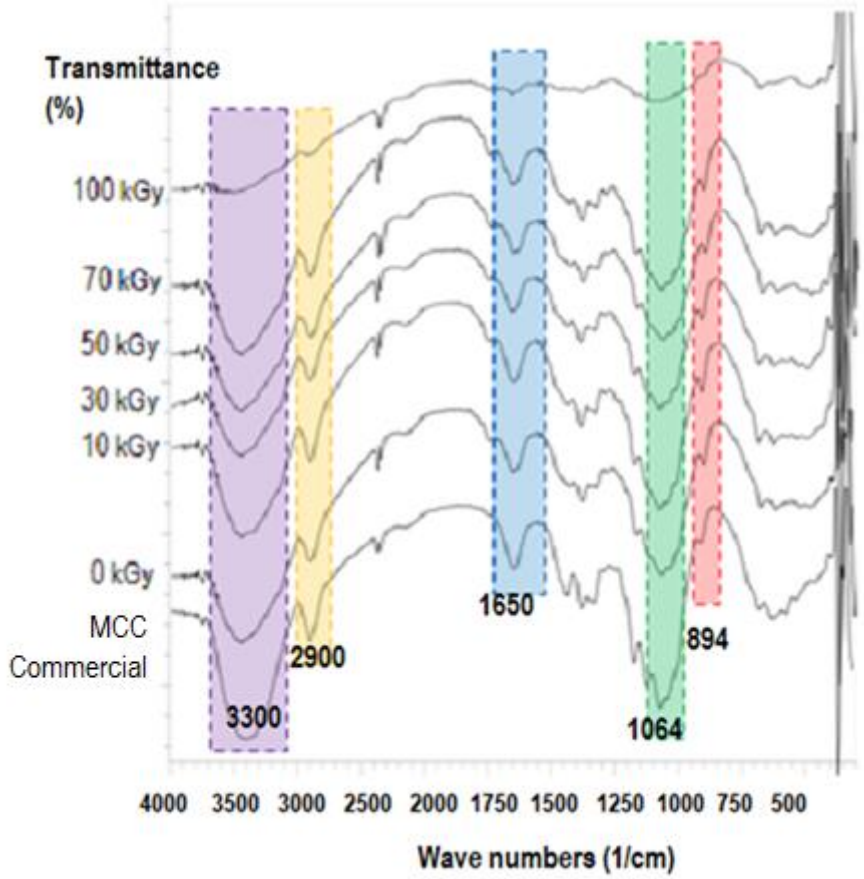

Fig. 1. FTIR spectra of cotton cellulose and MCC with various irradiation doses.

The effect of dried and wet medium phase gamma irradiation on FTIR spectra of MCC is presented in Fig. 2.

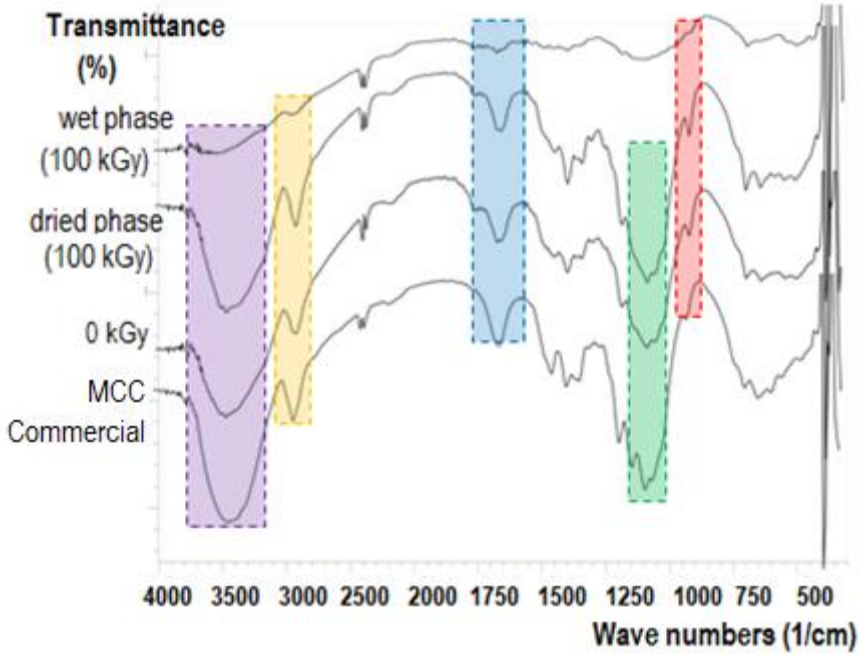

Fig. 2. FTIR spectra of MCC synthesized under dried and wet phase irradiation.

Compared to FTIR spectra of irradiated waste cotton fabrics synthesized under wet phase irradiation, dried phase irradiation exhibits only a slight decrease in peak intensity. In dried phase, cellulose could be

degraded due to a scission of glycosidic bond directly by gamma radiation. Irradiation of cellulose in a wet phase in the presence of hydrogen peroxide could increase cellulose degradation due to higher OH radical formation. Hydroxyl radical which is enhanced through radiolysis of H_2O_2 can increase cleavage of β-glycosidic linkages of cellulose. The similar synergetic effect is observed for degradation of chitosan with gamma radiation and hydrogen peroxide [23].

3.2. Characterization of Microcrystalline Cellulose Using X-ray Diffraction

X-ray diffractograms of waste cotton cellulose, MCC from irradiated cellulose, and MCC commercial are shown in Figs. 3, 4, and 5. All diffractograms exhibit main crystal planes of the crystalline cellulose I structure with the main characteristic peaks localized at 14^0, 18^0, 22^0 and 34^0 and diffraction patterns of MCC from irradiated waste cotton fabrics are almost similar to those of MCC commercial. After irradiating the waste cotton to a dose of 50 kGy in the wet phase, an increase in the crystallinity was observed in the XRD patterns which shows increasing peak intensity especially at 22^0 and is summarized in Table 1.

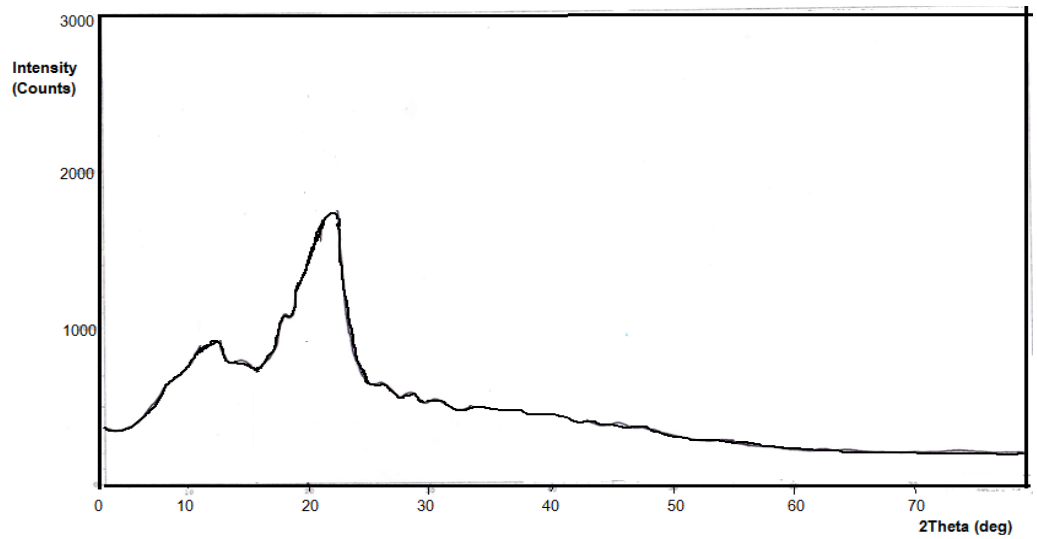

Fig. 3. X-ray diffractograms of waste cotton.

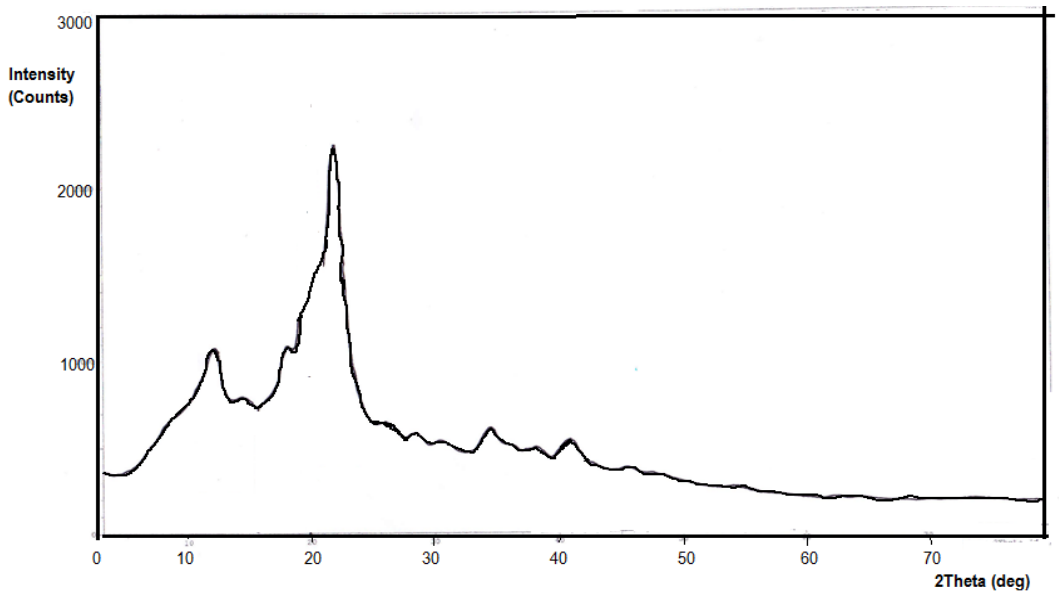

Fig. 4. X-ray diffractograms of MCC from wet phase irradiation 50 kGy.

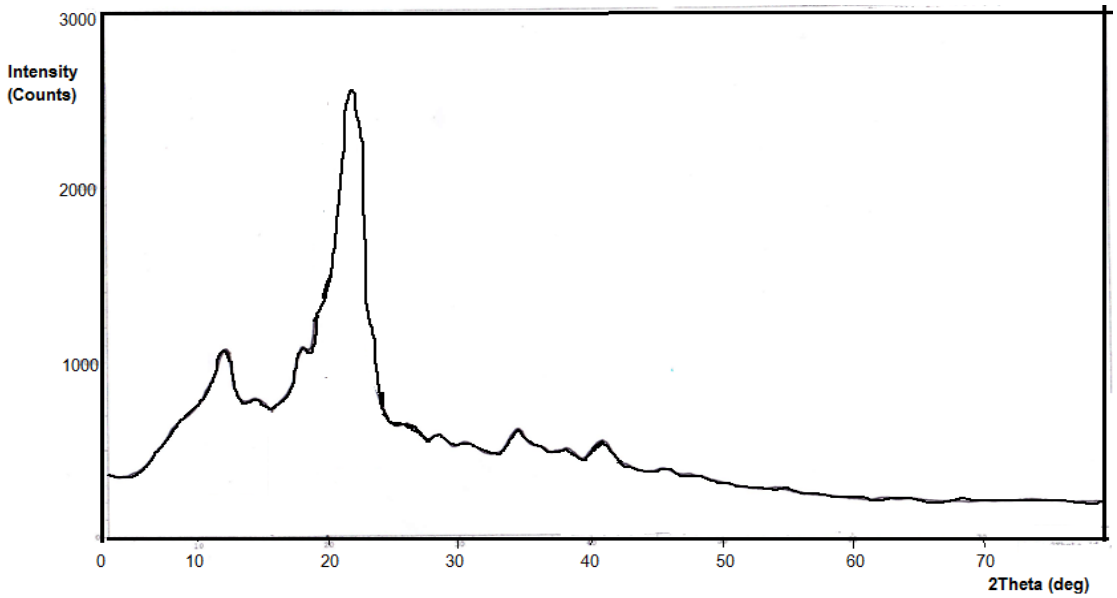

Fig. 5. X-ray diffractograms of MCC commercial.

Table 1. Crystallinity of waste cotton, irradiated waste cotton and MCC commercial.

Cellulose type	Percentage crystallinity (%)	Crystallite sizes (nm)
Waste cotton fabrics	62.63	5.92
MCC from 50 kGy irradiated waste cotton	70.80	4.65
MCC commercial	76.88	4.00

The percentage crystallinity of MCC from irradiated waste cotton fabric increased from 62.63 % to 70.80 %. It was also found that gamma irradiation slightly decreased crystallite size of cellulose. The resulting crystallinity of MCC is between the ranges for MCC commercial. In cotton cellulose structure, cellulose fibers are surrounded by hemicellulose and lignin structure. Increasing percentage crystallinity occurs due to degradation of the hemicelluloses, which is more amorphous than cellulose during irradiation. The amorphous part is more reactive to gamma radiation compared to the crystalline part because the cohesive energy density in the crystalline form is much higher than that for amorphous cellulose. Interaction of gamma radiation with hemicellulose is degradation by cleavage of glycosidic bonds between cellulose and hemicellulose with subsequent releasing individual crystallites that was confirmed by FTIR spectra. Tanvir et al [24] also observed the increasing crystallinity of irradiated cellulose film by gamma radiation at low radiation doses. Another study also obtained similar results while producing MCC from banana plant waste during the hydrolysis process, because part of the amorphous components was slightly removed due to scouring with an alkali solution [18]. However, the result published by Danu et al. [19] showed that degree of crystallinity of irradiated oil palm empty fruit bunch by electron beam decreased with irradiation dose up to 400 kGy. Furthermore, crystallinity of MCC derived from fibrillated cellulose was reduced from 87% to 45% with a radiation dose of 1000 kGy. At high radiation doses, interaction between ionizing radiation with cellulose might increase free radicals formation such that these radicals could also cause random cleavage chemical bonds of cellulose crystalline molecules.

3.3. Degree of Polymerization (DP)

Degree of polymerization describes the property of chain length of cellulose, expressed in numbers of constituents of anhydrous glucose. Figure 6 shows the dependence of the DP of cotton fabrics cellulose on gamma irradiation doses for wet phase irradiation.

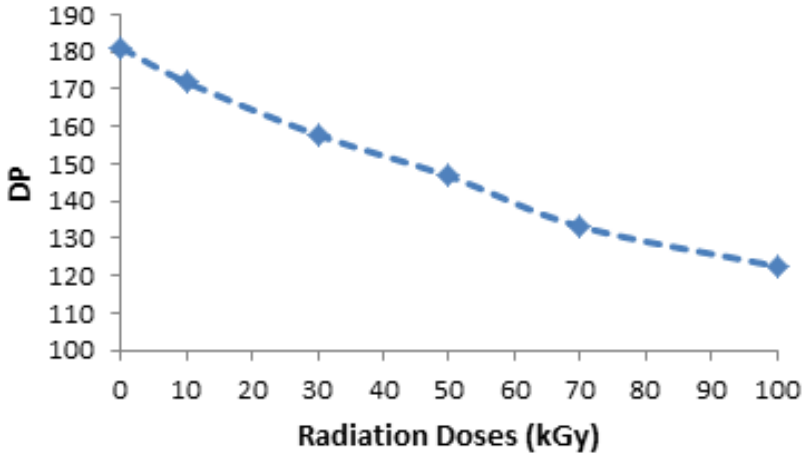

Fig. 6. Effect of radiation dose on the degree of polymerization of cellulose for wet phase irradiation.

It can be seen that DP of waste cotton cellulose decreased with an increase of gamma irradiation dose, indicating a decrease in molecular weight. DP reduction during gamma irradiation was due to direct chain scission at the β-glycosidic linkages, or an oxidation process following initiation caused by high energy radiation. Increasing irradiation dose increases reactive radicals by breaking of hydrogen bonds, thus reducing DP as confirmed by FTIR spectra. Similar results have been observed by Henniges et al. [13] that an increasing electron beam irradiation dose decreased DP of cellulosic materials.

The effect of dried and wet medium phase gamma irradiation on DP of MCC is shown in Table 2.

Table 2. Effect of medium phase irradiation on DP (100 kGy irradiation dose).

Type medium phase irradiation	Degree of polymerization
Wet medium phase	123
Dried medium phase	135

The result shows the dependence of the change in DP of waste cotton fabrics cellulose on the dried and wet medium phase irradiation. Decreasing DP is greater for gamma irradiation in hydrogen peroxide wet medium phase than for irradiation in dried phase. Cellulose degradation in dried state irradiation occurs through formation of macro radicals by the direct interaction. In aqueous solution, degradation of cellulose was probably due to the indirect effect of radiation by water radiolysis products rather than the direct effect of radiation. The free radicals such as hydroxyl radicals formed by radiolysis of water are effective even in enhancing of cellulose degradation. The presence of oxidizing or easily oxidized species such hydrogen peroxide is expected to enhance the formation of hydroxyl radicals and enhances the degradation process to reduce DP of cellulose.

3.4. Solubility in Water

The influence of gamma irradiation dose on the water solubility of cellulose in wet and dried medium phase is shown in Fig. 7 and Table 3. Water solubility of irradiated cellulose slightly decreases consequently to an increase in the gamma irradiation dose. Gamma irradiation on the polymeric structure causes some physical and chemical properties changing that are depending of the type of interactions with radiation [20, 25]. Solubility in water of cellulose depends on its DP, crystallinity, and active chemical groups such as hydroxyl groups.

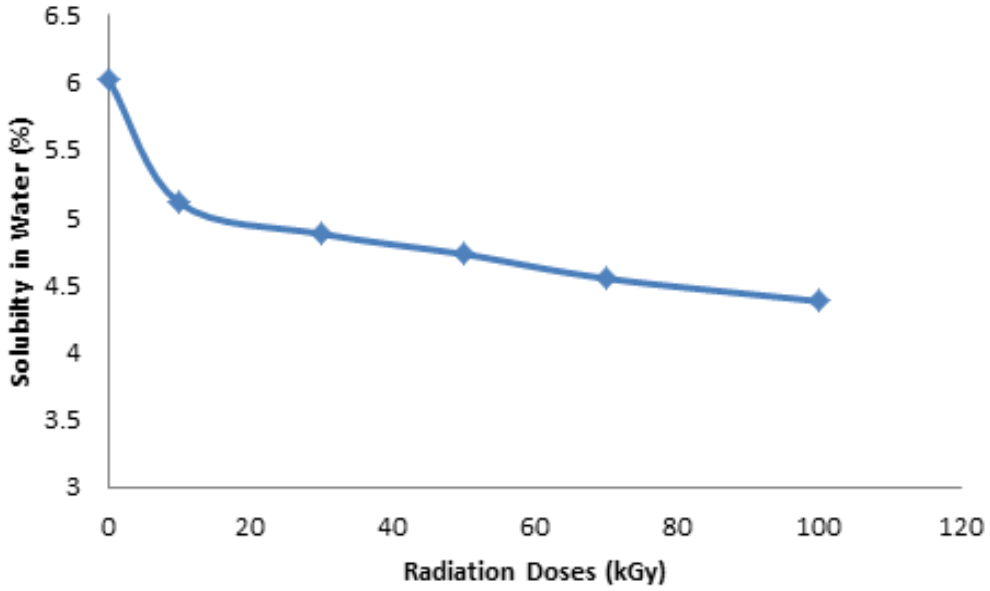

Fig. 7. Effect radiation dose on solubility in water of cellulose for wet phase irradiation.

Table 3. Effect of medium phase irradiation on solubility in water (100 kGy irradiation dose).

Type of medium phase irradiation	Solubility in water (%)
Wet medium phase	4.38
Dried medium phase	4.46

Based on the results, irradiation of waste cotton fabrics cellulose increased percentage crystallinity while DP and the hydroxyl groups in the cellulose decreased. Decreasing DP of cellulose increased the solubility in water because the molecular weight is reduced and this might increase the entropy driving force for dissolution due to decreasing number of intermolecular interactions. Increasing percentage crystallinity at a low radiation dose decreased the solubility because dissolving cellulose requires solvent molecules getting access into the core of cellulose crystalline. Irradiated cellulose exhibit a decreased number of hydrophilic character of hydroxyl groups as shown in FTIR results which tend to decrease the solubility of the cellulose. Based on the results, increasing cellulose crystallinity and decreasing polar hydroxyl groups play a more important role in cellulose solubility in water than decreasing DP.

3.5. Physicochemical Properties

The results of some physicochemical properties of the MCC prepared from irradiated waste cotton fabrics cellulose and the standard Avicel PH101 commercial carried out in accordance with European Pharmacopoeia are shown in Table 4. The results of the MCC from irradiated waste cotton showed that the MCC were white and granular powder. These results agree with MCC commercial and the European Pharmacopoeia (EP) specifications for MCC. The test for irradiated cellulose revealed that the pH did not change from the value of 5. The EP specified pH range of 5 to 7.5 for microcrystalline cellulose; therefore, the results complied with specifications for the pH of MCC.

Weight loss on drying was expressed as moisture content which could be an indication of suitability of the material for use as diluent. Table 4 shows that percent loss on drying determined on the MCC from irradiated waste cotton cellulose was found in the range of 5.39 to 6.19 %, being higher than Avicel MCC commercial i.e. 0.86 %. European Pharmacopoeia limit of loss on drying for MCC has been set at 7.0 %. These results indicated that the loss on drying of the all samples is within the specification. Bulk density of MCC reflects its porosity, which is an important factor in the application of MCC because it is used as an indirect method of assessing powder flow ability. As shown in Table 4, there are no significant differences on effects of the irradiation doses and medium phase irradiation on the bulk densities of the

microcrystalline cellulose samples. The bulk density for the MCC was slightly higher than that of the Avicel as seen in Table 4. Increased bulk density has been suggested due to small particle size and it also can be controlled by grinding process. An increase in bulk density might be associated with the better the potential for a material to flow and to re-arrange under compression [6]. The result revealed that all microcrystalline cellulose samples might have good flow properties.

Table 4. Physicochemical properties of the MCC and Avicel PH101 MCC commercial.

Parameters	Wet phase Irradiation					Dried phase	MCC Commercial	Requirements of European Pharmacopoeia
	10 kGy	30 kGy	50 kGy	70 kGy	100 kGy	100 kGy		
Colour	White	White	White	White	White	White	White	White
Texture	Granular powder	Granular powder	Granular powder	Granular powder	Granular powder	Granular powder	Granular powder	Granular powder
pH	5	5	5	5	5	5	5	5.0 – 7.5
Loss on drying (%)	5.39	5.57	5.71	6.11	6.15	6.19	0.86	< 7.0
Bulk density (gr/cm^3)	1.262	1.258	1.250	1.248	1.236	1.220	1.127	-

4. Conclusion

Microcrystalline cellulose has been successfully isolated from waste cotton fabrics using gamma irradiation. The results obtained from FTIR and XRD analysis confirmed that the irradiated cellulose exhibits similar patterns compared to those of commercial MCC. XRD confirmed a slight increase in percentage crystallinity while crystallite sizes decrease with gamma irradiation dose. Increasing total irradiation doses could decrease both the degree of polymerization and solubility in water. The result showed that irradiation in hydrogen peroxide aqueous medium could increase degradation of waste cotton cellulose. The microcrystalline cellulose product obtained from the waste cotton fabrics using gamma irradiation conformed to the physicochemical properties in the European Pharmacopoeia.

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