Surface Coating on Cotton Fabrics of New Multilayer Formulations Based on Superabsorbent Hydrogels Synthesized by Gamma Radiation Designed for Diapers

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ABSTRACT: In this work, superabsorbent formulations composed of two layers of hydrogels, prepared by gamma irradiation, were surface coated on cotton fabrics. The first layer, which is directly surface coated on cotton fabrics, was based on the copolymer hydrogel of 2-acrylamido-2-methylpropanesulfonic acid/2-dimethyaminoethyl methacrylate (AMPS/DEMA). The top layer was based on pure AMPS hydrogel. The different hydrogel layers were characterized in terms of thermal stability by thermogravimetric analysis and mechanical testing. In addition, the swelling of the different layers of hydrogels in water and urea solutions (as a solution resembling urine) were studied. The results showed that the multilayer hydrogels obtained displayed higher swelling in urea than in water, which is promising in the field of diapers.
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Key words: gamma irradiation; formulations; surface coating; thermal; swelling kinetics

INTRODUCTION

Radiation curing has become a well accepted technology, which has found a large number of industrial applications mainly in the coating and printing fields, in the manufacture of adhesives, and in microelectronics.[1] It allows the rapid transformation of liquid multifunctional monomers and oligomers into solid polymer coatings. The main advantages of irradiation technology over the conventional curing of coatings by chemical methods may be attributed to the use of solvent-free, 100% polymerizing binders with less hazard and environmental pollution, chain reaction curing initiated at low temperature. The formulation to be cured or crosslinked by irradiation usually contains unsaturated monomers (double bonds), oligomers, and other additives depending on the desired properties.[2]

UV and electron irradiation have been extensively used for curing formulations and oligomers applied by surface coatings on different surfaces for different purposes. Gamma-irradiation technology was used in combination with edible coating to produce shelf-stable foods.[3] Three types of commercially distributed food products were investigated; precooked shrimps, ready to cook pizzas, and fresh strawberries. Samples were coated with various formulations of protein-based solutions and irradiated at total doses between 0 and 3 kGy. Different synthetic fabrics were treated by electron beam surface coating with two formulations based on polydimethylsiloxane (PDMS) and polystyrene (PS) or poly(methyl methacrylate) (PMMA) oligomers.[4] The water resistance properties were investigated in terms of the percentage of water repellency and absorption. Also, the surface coated fabrics were examined by scanning electron microscopy/microscope (SEM) connected to an energy dispersive X-ray (EDX) unit to determine the percentage atomic contents of the elements. The results showed that the adhesion of the polysiloxane formulation to the surface depends largely on the kind of acrylate oligomer and textile fabric as indicated by the EDX analysis for silicon. In this regard, PDMS/PS formulation is more compatible with polyester and nylon-6 fabrics than PDMS/PMMA one. Pigment colors printing on cotton fabrics by surface coating induced by electron beam and thermal curing was also investigated.[5] Cotton fabrics were coated from one surface with different pigment colors incorporated in formulations containing ethylene glycol (EG), methyl methacrylate (MMA), and PMMA oligomer as a base material. The coated fabrics were exposed to various doses of accelerated electrons generated from the 1.5 MeV (37.5 kW) electron beam accelerator machine. The durability of the printed fabrics in terms of color fastness, tensile mechanical, crease resistance, and water absorption was studied. The results showed

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that cotton fabrics printed with the pigment colors under the effect of electron beam irradiation displayed higher color strength than those fabrics printed by the conventional thermal fixation at equal pigment color ratios. Recently, a novel coating formulation to impart ultraviolet (UV) protection property to cotton, poly(ethylene terephthalate) (PET), and cotton/PET fabrics was prepared and gamma rays as an ionizing radiation was utilized for surface curing.[6] Natural occurring aluminum potassium sulfate (Alum) was used individually and in binary coat with zinc oxide (ZnO) to induce the UV-blocking properties. It was found that using Alum (0.3 g/mL) caused a prompt increase in ultraviolet protection factor (UPF) over the uncoated fabrics.

As can be seen from literature, there is little work related to the current research in literature, except the work which is already demonstrated above. However, in these research works, the applied radiation curable formulations, by either gamma or electron beam, contain monomer and oligomers, which imparts the desired property to the coated fabric. In the present work, monomers only and no initiators were used. Gamma irradiation as a technique has an advantage of penetrating efficiency than electron beam irradiation; therefore in the present work, superabsorbent formulations composed of two layers of hydrogels were fabricated under the effect of gamma irradiation. The main objective of this work is to produce diapers based on thin layers of hydrogels compatible and to be surface coated on cotton fabrics. The vinyl monomers used in this study were 2-acrylamido-2-methylpropanesulfonic acid/2-dimethyaminoethyl methacrylate (AMPS/DEMA). The different hydrogel layers were characterized in terms of thermal stability by thermogravimetric analysis (TGA) and mechanical testing. In addition, the swelling in water and urea solutions, as a solution resembling urine, of the different layers of hydrogels were studied.

EXPERIMENTAL

Materials

AMPS monomer used in this study was of laboratory grade chemicals purchased from Alfa Aesar, GmbH & CoKG, Germany. DEMA monomer was of laboratory grade chemicals purchased from Merck Schuchartt OHG, Germany. The cotton fabric (plain weave) used throughout this work was kindly supplied by El-Nasr Spinning, Weaving and Knitting Co. (Shourbagi), Cairo, Egypt. It was scoured, bleached; however, before use it was washed with a solution containing 5 g/L of Na_2CO_3 and 1 g/L of detergent in water at 60°C for 60 min to remove any undesired materials.

Synthesis of hydrogels

The hydrogels were prepared by dissolving separately different ratios of AMPS and DEMA monomers in distilled water. The monomer solutions were then mixed with continuous stirring until complete miscibility was achieved. The ratios of AMPS and DEMA in the mixture were 80/20, 60/40, 50/50, 40/60, and 20/80%. The mixtures were then poured into test tubes and subjected to gamma irradiation. Prior to irradiation, the solutions were made free from oxygen by purging nitrogen gas for 5 min. Irradiation to the required doses was carried out in a ^{60}Co gamma cell (Russia) facility of the National Center for Radiation Research and Technology, Cairo, Egypt at a dose rate of 4.08 kGy/h. The different factors that may affect the formation of hydrogels were first studied. For the irradiation dose, it was observed that the appropriate dose that gives copolymer hydrogels based on AMPS/DEMA with measurable gel content was 2.5 kGy, whereas the dose of 2.5 kGy was enough to give complete gelation of pure AMPS.

Preparation of the first layer coated on cotton fabrics

For the first layer of coating, among the AMPS/DEMA ratios, the hydrogel ratio of AMPS/DEMA (20/80%) prepared at the dose 2.5 kGy of gamma irradiation was optimized and found easy to apply by surface coating and compatible with cotton fabric.

Preparation of hydrogel multilayer structures

Since AMPS monomer is very sensitive to gamma radiation and form crosslinked network structure even at low irradiation doses, it was chosen to form the top layer. It was also observed that the hydrogel based on pure AMPS cannot be used as a single layer for the design due to the complete gelation, which cannot be applied easily. Thus, AMPS monomer, in the appropriate liquor ratio, was first exposed to a dose of 2.5 kGy of gamma radiation to form a homogenous hydrogel. The hydrogel was dried and then ground to fine powder and sprayed homogenously on the AMPS/DEMA copolymer layer to form multilayer hydrogels structure. The whole structure was then exposed to a dose 12.5 kGy of gamma irradiation.

Determination of gel content

Samples of the prepared hydrogels were accurately weighed (W_0) and then extracted with distilled water using a soxhlet system for 6 h and then dried in a vacuum oven at 80°C to a constant weight (W_1).

The gel fraction is calculated according to the following equation:

$$\text{Gel}(\%) = [(W_1/W_0)] \times 100$$

Thermogravimetric analysis

The TGA thermograms were performed on a Shimadzu-50 instrument (Kyoto, Japan) at a heating rate of 10 °C/min under nitrogen flow (20 mL/min) starting from room temperature up to 500°C. The primary TGA thermograms were used to determine the kinetic parameters of the thermal decomposition reaction.

Tensile mechanical properties

Mechanical testing including stress and strain at break and yield points of AMPS/DEMA structures was preformed at room temperature using an Instron Machine (model 1195, England) employing a crosshead speed of 5 mm/min according to ASTM D-638 standards. The recorded values of the tensile strength and elongation at break and yield points are average of five measurements.

Swelling studies of hydrogels

Swelling studies were carried out in water and 4% urea aqueous solution as solution resembling the urine. A known dry weight of sample (W_d) was immersed in water or urea solution for different intervals of time at 25°C and pH 7. At each time interval, the sample was removed and blotted on filter paper to remove excess solution and weighed (W_s), in which the swelling in water or urea solution is calculated according to the following equation:

$$\text{Swelling}(\%) = [(W_s - W_d)/W_d] \times 100$$

RESULTS AND DISCUSSION

Radiation synthesis of AMPS/DEMA multilayer structures

In this work, AMPS and DEMA monomers were used to form hydrogel formulations under the effect of gamma irradiation. This is because AMPS and DEMA may provide a combination of superabsorbent properties based on the acrylamide, sulfonic acid, and amino groups. However, the main objective was to design a structure composed of two layers of materials; compatible and adherent with cotton fabric. The first one, which is directly coated on cotton fabric should be compatible and have viscosity property enough to be applied on cotton fabric by surface coating. Figure 1 shows the gel content of AMPS/DEMA hydrogels of different ratios, prepared at a dose 15 kGy. It is clear that the gel content decreases progressively by increasing the ratio of DEMA monomer in the initial feeding solution indicating the low sensitivity of DEMA monomer to radiation crosslinking and instead it undergoes oxidative degradation. The mechanism of network structure hydrogels formation based on pure AMPS or AMPS/DEMA (20/80%) copolymer hydrogels may be proposed to occur through two steps: both AMPS and DEMA monomers contain unsaturated C=C double bonds, which absorb gamma radiation resulting in the formation of free radicals. The copolymerization and crosslinking will proceed, in which two polymer radicals of AMPS and DEMA with "*n*" and "*m*" repeats units, respectively, combine to form a crosslinked points after which a network structure is formed as shown in Figure 2.

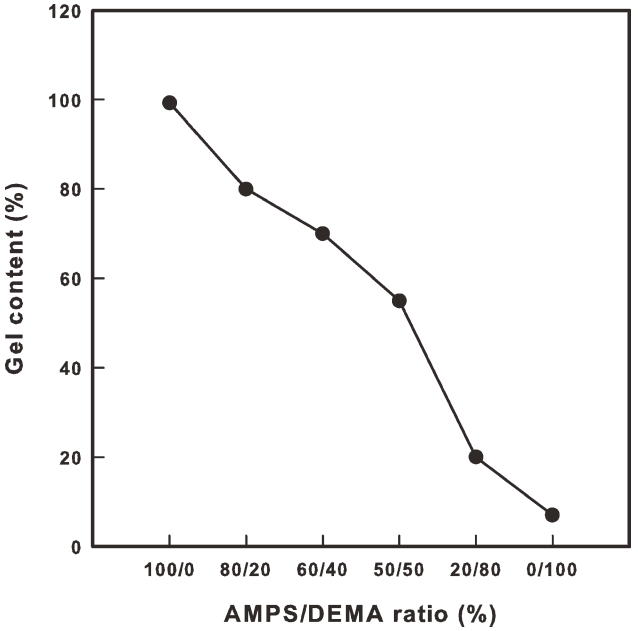

Figure 1 Gel content of different ratios of AMPS/DEMA hydrogels prepared at a dose of 15 kGy of gamma radiation.

Thermal decomposition of AMPS/(AMPS/DEMA (20/80%))/cotton multilayer structures

The average complete dissociation energies for the polymers based on the monomers AMPS and DEMA and based on the reported theoretical dissociation energies of the different covalent bonds forming the polymer molecules are calculated to be 403.4 and 409.9 kJ/mole, respectively.[7] Thus, it may be expected that the formation of copolymer hydrogels with increased DEMA ratio will eventually result in hydrogels with higher thermal stability than pure AMPS hydrogel. TGA was used to investigate the thermal stability. Figure 3 shows the initial TGA thermograms and the rate of thermal decomposition

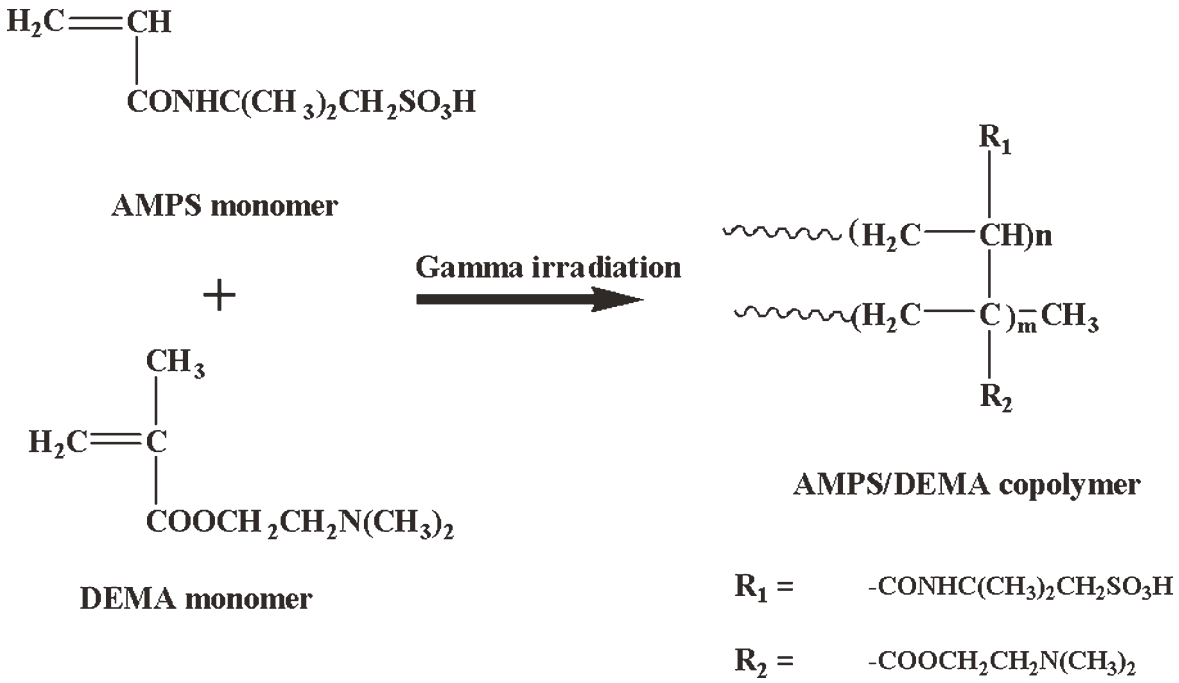

Figure 2 Possible mechanisms for the formation of network structure of AMPS/DEMA copolymer hydrogels.

reaction of hydrogels prepared at 15 kGy of gamma irradiation of solutions based on pure AMPS and AMPS/DEMA (20/80%). Overall, at the heating temperatures from 100°C up to 500°C, the AMPS/DEMA (20/80%) copolymer hydrogel displayed higher thermal stability (with low weight loss) compared to the hydrogel based on pure AMPS. The derivative of the TGA curves (rate thermal decomposition reaction) for either pure AMPS or AMPS/DEMA (20/80%) copolymer hydrogel showed multiple stage thermal decomposition as shown in Figure 3. The different kinetic parameters including T_{onset}, T_{endset}, and T_{peak} temperatures are shown in Table I. Based on the thermal decomposition study, it could be concluded that the thermal stability of AMPS/DEMA (20/80%) copolymer hydrogel is greater than that of pure AMPS hydrogel. Thus, the copolymerization of AMPS with DEMA increased the thermal stability of the final hydrogel.

Mechanical properties of AMPS and AMPS/DEMA hydrogels

Most plastic materials are used because they have desirable mechanical properties at an economic cost. For this reason, the mechanical properties may be considered the most important of all the physical properties of high polymers for most applications. There are many structural factors, which affect the mechanical behavior of such materials. In addition to the chemical composition, molecular weight, crosslinking and branching, crystallinity and crystal morphology, copolymerization, plasticization, molecular orientation and fillers are structural factors, which affect the mechanical properties. The stress–strain test is the most widely method used of all the mechanical tests.

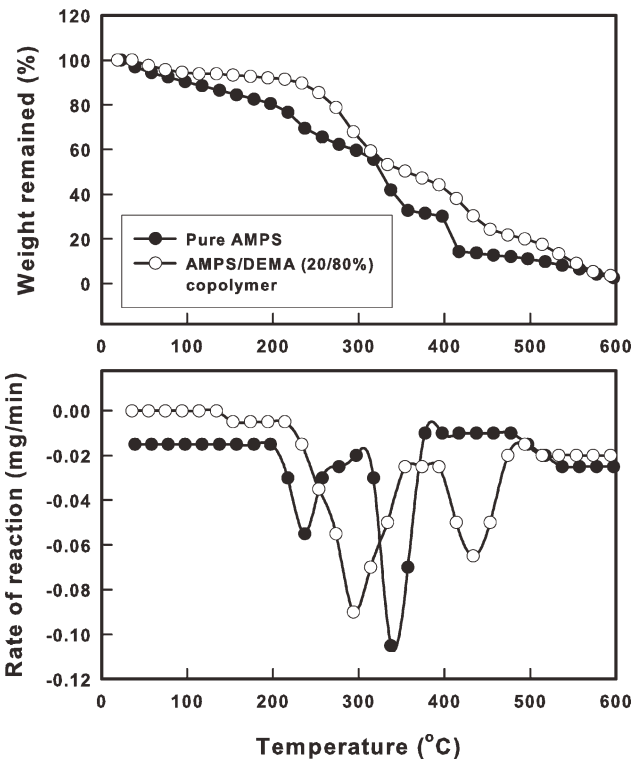

Figure 3 TGA thermograms and rate of thermal decomposition reaction of hydrogels based on pure AMPS monomer and AMPS/DEMA (20/80%) copolymer prepared at a dose of 15 kGy of gamma radiation.

TABLE I
Kinetic Parameters of the Thermal Decomposition Reaction of Hydrogels Based on Pure AMPS and AMPS/DEMA (20/80%) Copolymer Synthesized by Gamma Irradiation at a dose 15 kGy

Hydrogel structures	First peak of rate of thermal decomposition reaction			Second peak of rate of thermal decomposition reaction		
	T_{onset} (°C)	T_{endset} (°C)	T_{peak} (°C)	T_{onset} (°C)	T_{endset} (°C)	T_{peak} (°C)
AMPS (100%)	201	299	235	299	379	340
AMPS/DEMA (20/80%)	220	337	296	337	475	433

The tensile mechanical properties at yield and break points for the different AMPS/DEMA hydrogels structures were tested as shown in Figures 4 and 5. Cotton fabrics irradiated at a dose of 15 kGy displayed the lowest tensile strength at either yield or break points. However, the multilayer structure, which is composed of cotton fabrics as the base, coated AMPS/DEMA (20/80%) copolymer hydrogel and coated hydrogel based on pure AMPS, showed the highest tensile strength at either yield or break points. As shown in Figure 6, the strain at the yield point of cotton fabric was not affected by either adding the AMPS/DEMA (20/80%) copolymer hydrogel or the top layer based on pure AMPS. However, a different trend can be observed in case of strain at break point, in which the total structure displayed the highest value. The improvement in mechanical properties of the whole structure [AMPS/(AMPS/DEMA)/cotton fabric] after gamma irradiation is due to the occurrence of crosslinking and graft copolymerization of AMPS component. The surface coating of AMPS as flexible polymer on cotton/(AMPS/DEMA) structure would result in the formation of different reaction such as hydrogen bonding.

Swelling characters in water and urea

Figure 6 shows the swelling kinetics in water at 25°C (pH = 7) for the structure based on [AMPS/(AMPS/DEMA)/cotton fabric] gamma irradiated at a dose of 15 kGy. It can be seen that the swelling increased greatly within the initial time of swelling up to 100 min and then tends to level off up to 200 min. The swelling of the same structure in urea solution displayed similar trends; however the swelling in urea is much higher than the swelling in water. It is interesting to see that swelling of hydrogels in urine solution is much higher than in pure water. This is attributed to the fact that urine has more hydrophilic amide and carbonyl groups and it is known that urine is also denaturing agent.

As shown in Figure 6, the whole multilayer hydrogel structure based on [AMPS/(AMPS/DEMA)/cotton fabric] displayed higher degree of

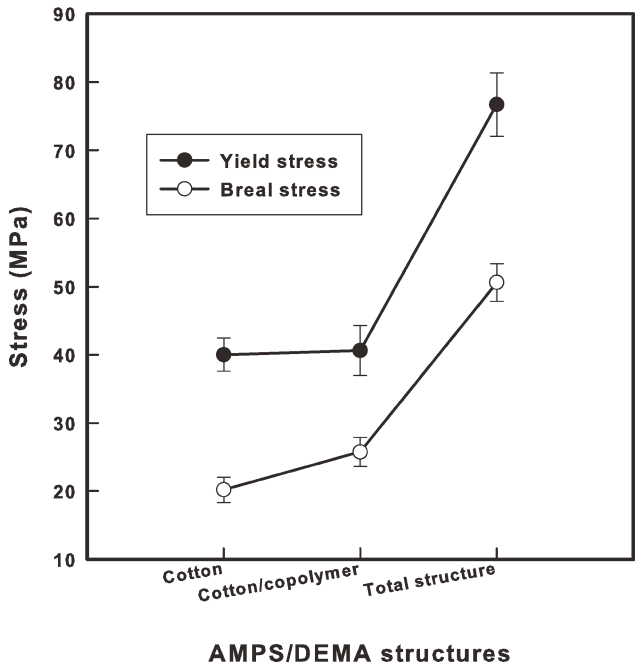

Figure 4 Tensile mechanical properties at yield and break points for different AMPS/DEMA hydrogel structures prepared at a dose of 15 kGy of gamma radiation.

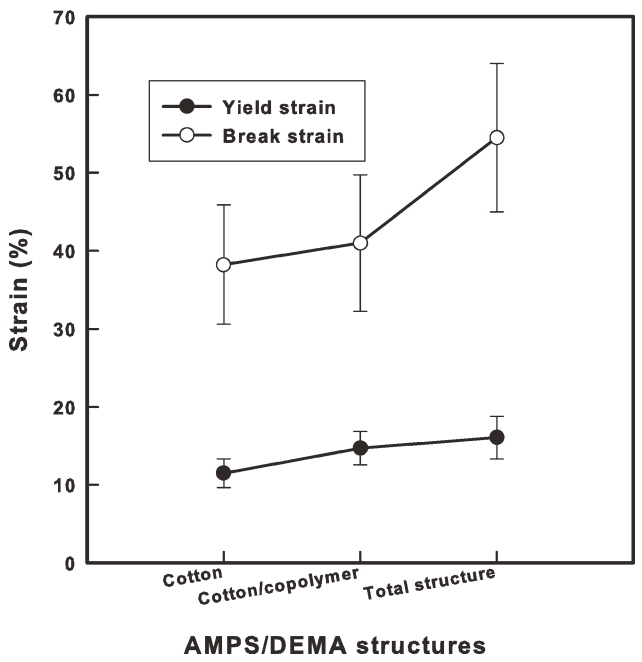

Figure 5 Elongation properties at yield and break points for different AMPS/DEMA hydrogel structures prepared at a dose of 15 kGy of gamma radiation.

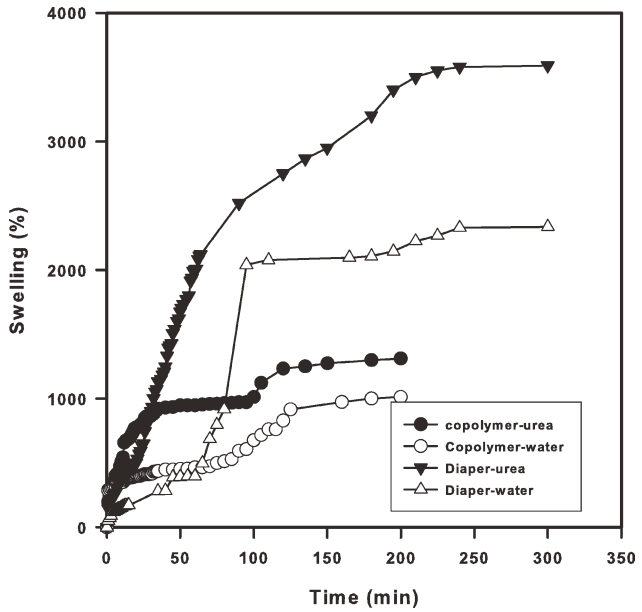

Figure 6 Swelling-time dependency in water and urea for the hydrogel structures (AMPS/DEMA) (20/80%) and [AMPS/(AMPS/DEMA)] applied by surface coating on cotton fabrics, prepared at 15 kGy of gamma irradiation.

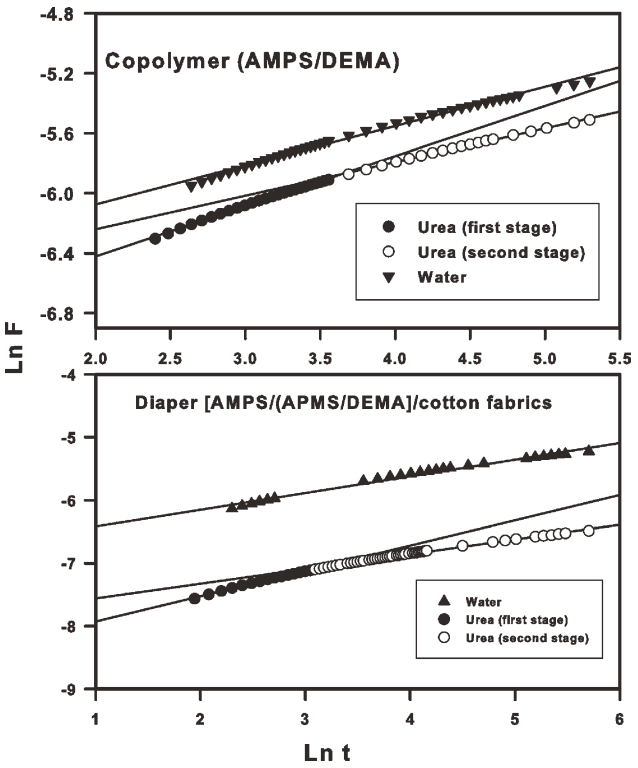

Figure 7 Plots of (ln F) against (ln t) of the swelling in water and urea for the copolymer hydrogel (AMPS/ DEMA) and diaper structure [AMPS/ (AMPS/DEMA)] applied by surface coating on cotton fabrics, prepared at 15 kGy of gamma irradiation.

swelling in water than AMPS/DEMA copolymer. The higher swellability of the total structure of hydrogels may be attributed to the higher hydrophilic character of AMPS in the networks due to the presence of acrylamido and sulfonic acid groups.

The nature of water and urea diffusion into different hydrogels structures was determined by applying Fick's law according to the following equation.[8]

$$F = W_t/W_e = Kt^n \text{ or } \ln F = \ln K + n\ln t$$

where F is the ratio between the amount of water absorbed by the hydrogel at time t (W_t) and the amount of water absorbed by the hydrogel at equilibrium (W_e), K is a constant characteristic of the structure of the networks and n is an exponent which determines the mode of water diffusion. When ln$F$ is plotted against ln$t$, it gives a straight line from which the intercept determines the constant K and the slope gives the number n. In this regard, a value of $n = 0.5$ indicates a Fickian diffusion mechanism in which the sorption is diffusion controlled, whereas a value of $0.5 < n < 1$ indicates an anomalous non-Fickian type diffusion and contributes to the water-sorption process. Figure 7 shows the application of the above equation to the different hydrogel structures and the calculation of the diffusion parameters is presented in Table II. The data indicate that all the hydrogels structures display a non-Fickian type of diffusion. Therefore, it can be conclude that the diffusion of water into the

TABLE II
Kinetic Parameters of Swelling in Water and Urea of Different Hydrogel Structures

	Swelling in Urea			Swelling in Water		
Hydrogel structures	n	$K \times 10^4$	r^2	n	$K \times 10^4$	r^2
(AMPS/DEMA)/cotton fabric						
First stage	0.34	8.322	0.997	0.26	13.64	0.9926
Second stage	0.22	12.45	0.997			
	n	k	r^2	n	k	r^2
AMPS/(AMPS/DEMA)/cotton fabrics						
First stage	0.40	2.421	0.996	0.27	12.5	0.985
Second stage	0.24	4.117	0.993			

hydrogel networks is not controlled but it depends on water sorption process, which in turn depends on the structure and pathways of water through the networks. In addition, it can be seen that there is a difference in n parameter value for swelling in water and urea for the hydrogels based on pure AMPS (100%) and AMPS/DEMA (20/80%).

CONCLUSIONS

A new efficient procedure is presented for surface coating of gamma radiation synthesized multilayer formulations on cotton fabric with the objective of designing diapers. In this respect, the thickness of multilayer structure is important. Based on the results obtained two conclusions may be made: (1) the multilayer structure, which is composed of cotton fabrics as the base, coated AMPS/DEMA (20/80%) copolymer hydrogel and coated hydrogel based on pure AMPS, showed the highest tensile strength at either yield or break points. (2) The swelling of the same structure in urea solution is much higher than the swelling in water.

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