Enhancing Water Resistance of Paper by Graft Copolymerization Reaction

S. M. Sayyah,[1] A. B. Khaliel,[1] E. H. Mohamed[2]

[1]Polymer Research Laboratory, Chemistry Department, Faculty of Science, Beni Suef University, 62514 Beni-Suef City, Egypt
[2]Polymer Research Laboratory, Chemistry Department, Faculty of Science, Beni Suef University, 62514 Beni-Suef City, Egypt
Correspondence to: S. M. Sayyah (E-mail: smsayyah@hotmail.com)

ABSTRACT: The chemical graft copolymerization reactions were used to enhance water resistance of paper by reaction of acrylonitrile (AN) monomer onto cellulosic paper sheet in the presence of comonomer (styrene or acrylic acid or itaconic acid) 1 : 1 molar ratio in dimethyl formamide using benzoyl peroxide as free radical initiator under nitrogen atmosphere at 70°C. The infrared spectroscopy confirms that graft copolymerization reaction occurs onto the paper samples. Water absorption test was carried out following the Normal Protocol 7/81 (water absorption by complete immersion) to evaluate the protective effect of the graft treatment onto the paper sheet. It was found that the three graft copolymerization systems reduced the water absorption of the investigated paper and the reduction of water absorption is directly proportional to the grafting %. The wettability of the grafted and ungrafted paper sheet samples were investigated using the wicking time method which exhibits the decreasing of paper sheet wettability using the AN/S comonomers in the graft copolymerization reaction. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

A paper-based product typically contains 90–99% cellulose fibers which are the primary structural element and the most important component influencing the properties after being used. A network of self-bonding cellulose fibers within network structure affects chemical and physical characteristics of the paper products. However, the chemical structure of cellulose is now well established and consists β-anhydroglucose units with dominant hydroxyl groups, which are appropriate groups for reactions. These are mainly due to the one primary and two secondary hydroxyl groups in each monomer unit in the polymer structure.[1,2]

The pore network is inextricably involved with the fibrous paper structure.[3] Therefore, paper can be described as a two-phase material of pore filling phase and solids.[4] Porosity is regarded as the most important single structural feature of paper.[5] The three dimensional (3D) pore structure directly governs the density and optical properties of paper.[3] Porosity, pore size distribution, and pore tortuosity largely control the liquid transport in paper.

The porosity and pore topology of the fiber web, including fiber micropores and cracks, play an important part in the liquid imbibition's phenomenon. Cellulose is hydrophilic and swells when interacting with water.[6]

Graft copolymerization reaction of vinyl monomers onto cellulosic fibers is a subject of intense studies; in some cases, remarkable changes in the physicochemical properties of the grafted fibers have been demonstrated. Specifically, grafting of a hydrophobic styrene monomer onto cotton fibers yielded a graft copolymer of improved resistance to wetting.[7]

Mcdowell et al.[8] stated that by chemical modification of cellulose through graft copolymerization with synthetic monomers many different properties, including water sorbency, elasticity, ion-exchange capabilities, thermal resistance, and resistance to microbiological attack can be improved. The grafting of hydrophobic monomers such as acrylonitrile (AN)[9,10] and methyl methacrylate[11,12] resulted in a decrease of water sorbency.

Water-retention capacity (WRC) for a cellulose vinyl monomer graft has been reported for hydrophilic and for hydrophobic vinyl monomers.[13] For hydrophobic monomers, the WRC of grafted fibers is expected to decrease with the increase of the graft yield.

Eighodalo and Arihanatu[14] stated that a threefold increase in the graft yield of a kenaf fiber-polymethacrylonitrile graft copolymer results in an 85% reduction in the WRC of the graft copolymer.

Khullar et al.[15] studied water sorbency of the parent and grafted cellulosic material derived from bamboo (*Dendrocalamus strictus*) expressed as water-retention value (WRV) in grams of water per gram of the oven dry sample according to the method described by Das et al.[16] He reported that the WRV of the parent cellulosic material sample was 12.2 g/g and of the grafted sample was 9.1 g/g. The WRV decreases on grafting indicating increased hydrophobic nature of the fibers on grafting. These findings are in good agreement to those reported by Das et al.[16]

Contact angle measurements on paper are always subject of discussions regarding their reliability since the papers are rough, porous, and inhomogeneous. These limitations affect the magnitude of contact angle resulting in contact angle hysteresis,[17] if contact angle between the liquid and paper is less than 90°. This affects the measurement of static contact angle on paper surface.

In many practical applications, the dynamic conditions are of greater importance than the static conditions. Consequently, the dynamics of wetting have attracted a considerable research interest over the last ten decades.[18,19]

The aim of the present work is to use the water absorption test according to Protocol 7/81 (Water absorption by complete immersion) and wicking time method which was proposed by Cuong et al.[20] to evaluate the protective effect of the graft treatment onto the paper sheet against water, where the surface structure and surface energy had been altered in a controlled way.

EXPERIMENTAL

Materials

The paper sheets (A4) Japan NPI; grammage 80 g/m^2 made largely from mechanical pulp which contains bleached cellulose, a noticeable amount of fillers ($CaCO_3$) (ash 18%). The paper sheet was cut into small pieces 2.5 × 2.5 cm^2 and 0.1 cm thickness. The paper sheets were treated with different polar and non-polar solvents to remove any fats from the paper sheet surface or organic additives present in the paper structure or polymeric additives.

AN was a product of Kock light Company (England). The monomer was washed with a few drops of 10% sodium hydroxide solution followed by small amount of distilled water, then the monomer was fractionated using a fractionating column of 15 theoretical plates. The fraction which boils at 77°C was collected and used.

Styrene (S) was a product of Merck, Germany, it was freed from the inhibitor by washing with 5% NaOH solution followed by distilled water, separated with a separating funnel, and after drying over anhydrous sodium sulfate it was distilled under vacuum.

Acrylic acid (AA) was a product of Merck (Germany), it was distilled under vacuum at 60°C/15 mmHg. The purified monomers were subsequently stored at a low temperature (4°C) and in the dark.

Methylenesuccinic acid [itaconic acid (IA)] was a product of Merck (Germany) purified by twice crystallization from distilled water.

The initiator for the free radical graft copolymerization reactions was benzoyl peroxide (BPO) provided from El-Nasr pharmaceutical chemical company, Egypt. It was purified and activated by dissolving in chloroform, then filtered, dried and kept under vacuum.

Ferrous ammonium sulfate hexahydrate (FAS), acetone, 1,4-dioxane, were products of B.D.H Chemical Company, England; dimethylformamide (DMF), chloroform, benzene, and methanol were of chemical pure grade from El-Nasr Pharmaceutical Chemical Company, Laboratory Chemical Division, Egypt. Deionized and distilled water was used throughout the present study.

Graft Copolymerization Reactions

The paper sheet samples were washed with distilled water, benzene, and methanol, then dried over anhydrous calcium chloride to remove the loosely adhering materials. It is also to break down the extensive hydrogen bonding between the OH groups of cellulose and open up the order regions, so that the reagents and monomers could easily penetrate inside the cellulose substrate. Also, the washing process leads to more activation of hydroxyl groups on cellulose surface in which the efficiency of grafting depends crucially on the available amount of these groups. The samples were dipped in FAS (0.02M) for 20 min then dried till constant weight. Glass manufactured quikfit tubes of 20 cm length and 40 mm diameter equipped with glass stopper were used as a reaction vessels for the graft copolymerization reaction. The reactions were carried out using binary mixture of the vinyl monomers as 2.079M, 1.860M, and 4M for (AN, S), (AN, AA), and (AN, IA) system, respectively, in which the monomer feed ratios of AN and the other monomer for each system were kept constant (1 : 1) using 0.0248M BPO as a free radical initiator at 70°C under nitrogen atmosphere for (2,3), (2) and (2,5) h, respectively. At the end of the graft copolymerization reaction, the paper is picked up and washed several times with acetone in case of (AN-S and AN-IA) systems and with 1,4-dioxane followed by DMF in case of the (AN-AA) system. The grafted paper is soaked in acetone or 1,4-dioxane for 24 h for complete extraction of the ungrafted copolymer present on the paper surface then dried for constant weight. The grafting % of each experiment was calculated as follows:

$$\text{Grafting\%} = [(W_1 - W_0)/(W_0)] \times 100 \qquad (1)$$

where: W_1 is the weight of the grafted paper sheet after the extraction of the ungrafted copolymer, W_0 is weight of the activated paper sheet before the graft copolymerization reaction.

Grammage—Basis Weight Measurements

Grammage is defined as the weight in grammes per unit area of paper or board .It is usually measured in the laboratory on an air-dry basis. In the USA the term "basis weight" is used whilst the term grammage is widely used and accepted.

The grammage of the investigated paper sheet samples have been measured in the metric system by weighing a known area of (10) replicated paper sheets (25 × 25 mm^2) for each sample after conditioning in a standard atmosphere for a set period of

time, according to TAPPI standard T 410 om—88 weight of paper sheet samples after heating for 3 h at 105°C.

Infrared Spectroscopy

The FTIR spectra of paper sheet, formed copolymer in the reaction medium, and the paper graft copolymerized with comonomers were recorded with a FTIR Jasco 460 plus spectrometer (Japan). Paper samples were analyzed in transmittance, with accumulation of 16 scans and a resolution of 4 cm^{-1}. In this case, approximately 1 mg of sample was used for the pellet preparation with 60 mg KBr. Firstly, to reduce the humidity content in the cellulose, a thermal treatment of pellets in oven at 80°C for 2 days was carried out.[21]

Scanning Electron Microscopy

The investigation of the surface morphology of the paper sheet before and after grafting reaction by different monomer pairs was carried out using JSM-T20 scanning electron microscope (SEM), JEOL, Japan. For better electric conductivity, the paper sheet surface was coated with thin gold layer before the examination photographs were taken at 1000 magnification.

Mechanical Properties of Paper

Since the physical properties of the paper change with the variation of moisture content, it is necessary to standardize it at a definite temperature and humidity values in order to obtain a standard test results. The samples were preconditioned for 24 h and tested at 65% relative humidity (RH) and 25°C.

Strength Properties. The tensile break load in (kg) is measured by a L Loyd L R10 universal testing machine. A paper strip of 15 mm width is clamped between two jaws and an increasing load is applied by swinging pendulum from its vertical resting position by a motor. The load causes the clamps to move apart until the strip breaks is the tensile break load in (kg), in this study the paper samples tested for tensile strength in machine direction.

Bursting Strength. Bursting strength was conducted according to TAPPI standard 403. A Mullen tester (Perkins, Chicopee, MA) was used. The burst strength in N/mm^2 is given as the pressure at which the paper sheet bursts.

Tear Resistance. The internal tearing resistance is measured by pendulum type instrument (Elenendorf Tear tester) which measures the amount of work done in tearing the paper through a fixed distance after the tear has been started by means of cutter attached to the instrument. For reporting the tear resistance results, the scale attached to the pendulum is graduated from 0 to 100, the ratio of the work done (g cm) to the total tearing length. The tearing resistance is the average force in grams required to tear the sheet clamped in the tester. In this study, the paper samples were tested for tear resistance across machine direction (Tear resistance = reading × 16/number of sheets) g cm.

Brightness. The amount of reflectance of so many sheet pads of paper that no change in reflection occurs when a backing is used is called R_∞. This is the intensity of light designated to the brightness of papers compared to the intensity of light reflected by a standard white body at the same wave length. The apparatus used in this work for measuring the brightness was a "Hunter lab instrument." The intensity of reflected light is measured photoelectrically.

Determination of the Water Absorption and Water Absorption Capacity

Most often, the dynamics of water sorption process has been investigated either by monitoring the change in physical dimensions of the substrate or by knowing the amount of water imbibed by the substrate at various times. In the present work, the later procedure was followed. To evaluate the protective effect of any conservative treatment onto the writing materials, a water absorption test or a water absorption capacity test was carried out. In this study, test was carried out at room temperature on six specimens of dimensions 2.5 × 2.5 cm^2 of each sample (pure ungrafted and different grafted paper sheet samples) and to ensure reproducibility, following the Normal Protocol 7/81 (Water absorption by complete immersion). First the specimens were dried in a vacuum oven at 50°C for 24 h, and then cooled in a desiccator then immediately weighed. The conditioned specimens were soaked in deionized water; the amount of water absorbed was determined by weighing the specimen as quickly as possible after 15, 30 min and 1, 1.5, 2, 4, 16, 24, and 48 h, to obtain the wet specimen (0.0001 g) using sensitive analytical balance after removing the surface mass water by adsorbing gently in-between two filter papers. The water absorption values were taken as an average of the six specimens of each sample. The amount of absorbed water Q_i, at the time t_i is defined as:

$$Q_i\% = [(M_i - M_o)/M_o] \times 100 \qquad (2)$$

where M_i is the specimen mass (g) at the time t_i and M_o is the dry specimen mass (g). The Q_i values were plotted against time to give the water absorption curve; and the amount of absorbed water at equilibrium state indicate water absorption capacity of the specimen. Comparing untreated and treated papers, a significant protective effect onto paper can be evaluated.

Determination of the Wettability by Wicking Technique

The wettability of the grafted and ungrafted paper sheet samples was determined with the use of wicking time method, which was proposed by Cuong et al.[21] According to this method, a droplet of distilled water as a wicking liquid was introduced on the grafted surface by a micro syringe and time for the droplet completely loosing its reflective power was measured .The paper samples dried at 100°C for 1 h and kept in a desiccator for 5 days and the tested samples were allowed to equilibrate for 12 h in a closed vessel with the saturated water vapor. The paper sheet samples were placed in a horizontal position in a controlled humidity chamber to prevent evaporation of the water droplet, enabling measurements over extended periods of time. The humidity chamber, made from Plexiglass, was transparent to light to allow the determination of the time at which the droplet completely loses its reflective power. The humidity inside the humidity chamber was controlled in the range of 95–99%. A drop size of 4 µL was introduced for each measurement and the temperature was held constant at room temperature (25°C).

For every grafted and ungrafted paper sheet sample at least 10 measurements were made in which the distilled water was dropped onto at least ten different sites on each sample, the

Table I. Values of Paper Sheets Grammage After Graft Copolymerization Reactions with Different Monomeric Pairs

Comonomers used for grafting reactions	Grafting reactions time (h)	Average grammage (g/m^2)	Grafting % after extraction of free copolymer	Average increase in the grammage (g/cm^2)	Name of the grafted product
AN/S	2	93	16	13	Paper gr-co-AN-S-2h-16%
AN/S	3	95	19	15	Paper gr-co-AN-S-3h-19%
AN/AA	2	91	14	11	Paper gr-co-AN-AA-2h-14%
AN/IA	2	86	8	6	Paper gr-co-AN-IA-2h-8%
AN/IA	5	88	10	8	Paper gr-co-AN-IA-5h-10%

extrapolated time corresponding to a 10 measurements was then obtained. An average time value was finally calculated from all the experiments for each paper sample.

RESULTS AND DISCUSSIONS

Grammage—Basis Weight Measurements
The average grammage for the original ungrafted paper sheet is 80 g/m^2; this value increases after grafting. The graft copolymer-

ization reaction allowed introducing copolymer onto the paper (graft %) which means an increase in grammage as shown in Table I. From Table I, it can be noted that a grammage of the paper sheet increases after graft copolymerization reaction, depending on:

- The time of the graft copolymerization reaction to (a limit extent), i.e., the average grammage of paper gr-co-AN-S-3h > average grammage of the paper gr-co-AN-S-2h.

Table II. Infrared Absorption Bands and Their Assignments of the Prepared Grafted Paper Sheet with Different Comonomer Pairs

| Wave number (cm^{-1}) Investigated samples				
	Graft paper sheet with different comonomer (pairs)			
Paper	AN/S	AN/IA	AN/AA	Assignments
470^{wv}	474 ^{vw}	479^w	464 ^{w}	C—C bending vibration
490^w	–	–	–	
560^w	578 ^{w}	–	570^b	C—C skeletal deformation
615^w	–	617^w	–	
665^w	–	–	–	
709^w	703^m	705^w	703^w	(CH$_2$) in plane rocking vibration mono substituted benzene ring
–	755^m	–	–	
875^m	879^w	881^w	879^w	In plane C—C—O str. Vibration
1056^b	1037^m	1056^w	1041^b	(C—O—C) str. Vibration or (C—C—O) out of plane str. In cellulose moiety and out of plane bending or C—N str. Vibrations
1112^m	–	1114^w	–	
–	–	–	–	
1162^w	1160^m	1164^w	1162^w	
1432^s	1440^b	1448^b	1428^b	CH$_2$ asymmetric bending vibration
1639^b	1635^m	1641^m	1643^m	Bound H$_2$O vibration in paper or corresponding to benzene ring
–	–	1739^s	1725^s	C=O str. vibration in COOH group
–	2238^m	2240^w	2246^w	C=O str. vibration
–	2859^w	2859^w	2862^w	(CH) alphatic asymmetric stretching vibration
4917^b	2923^m	2923^m	2921^m	
–	3060^w	–	–	CH aromatic str. Vibration
–	–	–	–	
3430^b	3426^b	3428^b	3428^b	Stretching vibration of H- bonded (OH) group
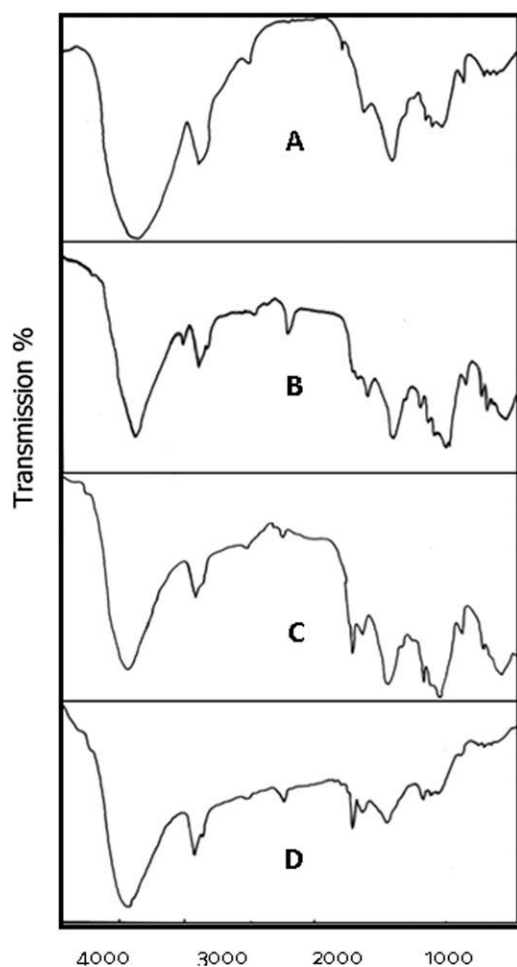
Figure 1. Infrared absorption spectra of (A) ungrafted paper sheet, (B) paper gr-*co*-AN-S, (C) paper gr-*co*-AN-AA, (D) paper gr-*co*-AN-IA.

- The nature of the introduced copolymer, i.e., by using FAS for activation The following order can be obtained: the average grammage of paper gr-*co*-AN-S-3h > average grammage of the paper gr-*co*-AN-S-2h > average grammage of the paper gr-*co*-AN-AA-2h > average grammage of the paper gr-*co*-AN-IA-5h > average grammage of the paper gr-*co*-AN-IA-2h.

Infrared Spectroscopic Analysis

Infrared (IR) spectroscopy is one of the most useful methods to detect the surface composition, from which the surface structure changes can be interpreted. The analysis led to confirm that graft copolymerization reaction occurs onto the paper samples, our investigations were performed with the ungrafted and the different obtained grafted paper samples at the optimum condition after 2 h. The infrared absorption bands of the ungrafted paper sheet and the grafted paper with different monomeric pairs and their assignments are summarized in Table II.

The IR spectra are represented in Figure 1(A–D), from which, the distinctive absorption bands could be found confirming the graft copolymerization reaction that occurs onto the paper samples are as follows:

1. The infrared spectrum of Paper gr-*co*-AN-S-2h-16% shows the absorption bands appearing at 703 and 755 cm^{-1} which could be attributed to the mono-substituted benzene ring of styrene. The band appearing at 2238 cm^{-1} could be attributed to the CN group. The medium band appearing at 3060 cm^{-1} may be attributed to the aromatic CH stretching vibration and the broad band appearing at 3426 cm^{-1} is attributed to the stretching vibration for H-bonded OH group [c.f., Figure 1(B)].
2. The infrared spectrum of Paper gr-*co*-AN-AA-2h-14% shows the absorption bands appearing at 1162 and 1724 cm^{-1} which are attributed to the C—O and C=O stretching vibration in COOH group, respectively, at 2246 cm^{-1} which is attributed to the CN group and at 3428 cm^{-1} which is due to the stretching vibration for H-bonded OH group [c.f., Figure 1(C)].
3. The infrared spectrum of Paper gr-*co*-AN-IA-2h-8% shows the absorption bands appearing at 1164 and 1739 cm^{-1} which could be attributed to the C—O and C=O stretching vibration in COOH group, respectively, at 2240 cm^{-1} which is attributed to the CN group. The band appearing at 3428 cm^{-1} is attributed to the stretching vibration for H-bonded OH group [c.f., Figure 1(D)].

Scanning Electron Microscopy for the Paper Sheet Before and After Graft Copolymerization Reaction with Different Monomer Pairs

The scanning electron micrographs of the paper sheet before and after graft copolymerization reaction by different monomeric pairs are shown in Figure 2(A–D). It is clear that in the micrographs of ungrafted paper sheet, some open fibrils in the inner layers of cellulose are visible [Figure 2(A)], while Figure 2(B–D) shows the surface morphology of the paper sheet after graft copolymerization reaction using different monomeric pairs of AN/S, AN/IA, and AN/AA, respectively. Regarding the figures, it is clear that some polymer chains are incorporated into cellulose fibers. The fibers in the inner layers of cellulose become invisible in which the polymer swells the fibers while cellulose fibers appear partially covered by copolymer as shown in the figures, the fiber boundaries are to some extent smoothened due to the coating of the open fibrils after grafting.

White crystals on different grafted paper sheet samples can be observed. This can be explained by the formation of calcium sulfate from (FAS) solution used for activating of the paper surface before graft copolymerization reaction. The crystals are clearly visible on the grafted paper surface and the amounts of these crystals are relevant because the quantity of CaCO$_3$ as filler in the investigated paper sample is high (about 18%). This phenomenon could also be seen due to the self-polymerized monomeric pair.

Mechanism of Graft Copolymerization Reaction onto Cellulosic Paper Sheet

The heterogeneous nature of the system causes same complications and uncertain trends for the present grafting. On the basis of the mechanisms suggested in the literature under nitrogen atmosphere using various redox systems in aqueous medium, we propose the following mechanism for graft copolymerization
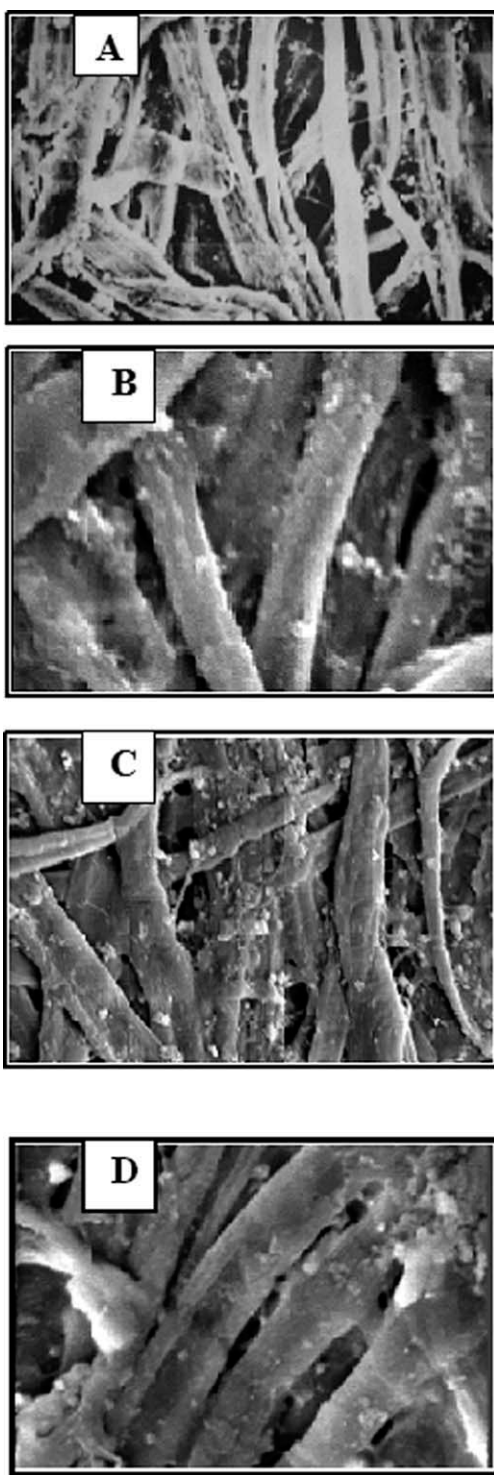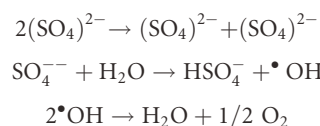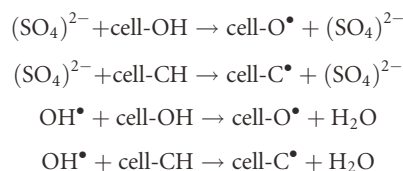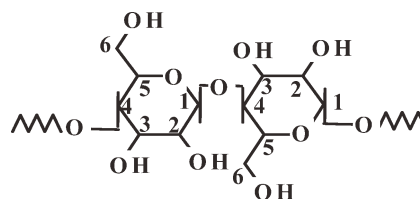
Figure 2. Scanning electro-microscopy pictures showing the morphology of the paper sheet. (A) paper ungrafted sheet, (B) paper gr-*co*-AN-S-3h-19%, (C) paper gr-*co*-AN-IA-5h-10%, (D) paper gr-*co*-AN-AA-2h-14%.

of AN monomer in the presence of the comonomer (S, AA, or IA) onto cellulosic paper sheet using aqueous solution of FAS followed by initiation of the reaction with Bz_2O_2. It has been found that, sulfate radical SO_4^{2-} is able to form free radical on compounds which contain hydroxyl groups.[22]

Activation

$$2(SO_4)^{2-} \rightarrow (SO_4)^{2-} + (SO_4)^{2-}$$

$$SO_4^{--} + H_2O \rightarrow HSO_4^- + {}^{\bullet}OH$$

$$2{}^{\bullet}OH \rightarrow H_2O + 1/2\ O_2$$

The free radical in case of cellulose backbone can be found to be formed by removal of one electron or more H atoms. It has been observed[23] that, polymeric materials containing cellulose C_2, C_3 and C_6—OH groups and C—H sites are the active centers for grafting of polymeric chains onto cellulosic backbone. The cellulose structure, as well as its numbered carbon atom, is represented in the following scheme
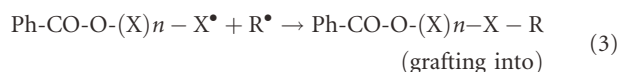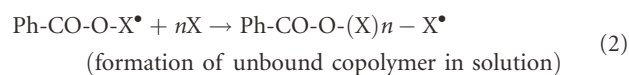

$$(SO_4)^{2-} + cell\text{-}OH \rightarrow cell\text{-}O^{\bullet} + (SO_4)^{2-}$$

$$(SO_4)^{2-} + cell\text{-}CH \rightarrow cell\text{-}C^{\bullet} + (SO_4)^{2-}$$

$$OH^{\bullet} + cell\text{-}OH \rightarrow cell\text{-}O^{\bullet} + H_2O$$

$$OH^{\bullet} + cell\text{-}CH \rightarrow cell\text{-}C^{\bullet} + H_2O$$

where cell–$O^{\bullet}$ and cell–$C^{\bullet}$ are cellulose free radical that can be formed, which take the symbol R·in the following steps.

Initiation. With the aid of the Bz_2O_2 radicals in the reaction medium, the monomer molecules (X) which are in close contact to the cellulose radical sites of reactions causing the grafted chain to grow.

$$R^{\bullet} + X^{\bullet} \rightarrow R - X^{\bullet}$$

$$R - X^{\bullet} + nX \rightarrow R - (X)n - X^{\bullet} \text{ (grafting from)} \quad (1)$$
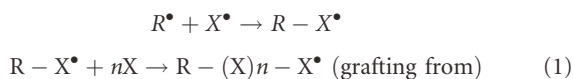
Also the monomer molecule (X) become acceptors of the Bz_2O_2 radical in the reaction medium and thereafter themselves become free radical donors to the neighboring molecules

$$X + Ph\text{-}CO\text{-}O^{\bullet}(\text{free radical of } Bz_2O_2) \rightarrow Ph\text{-}CO\text{-}O\text{-}X^{\bullet}$$

$$Ph\text{-}CO\text{-}O\text{-}X^{\bullet} + nX \rightarrow Ph\text{-}CO\text{-}O\text{-}(X)n - X^{\bullet}$$
$$\text{(formation of unbound copolymer in solution)} \quad (2)$$

$$Ph\text{-}CO\text{-}O\text{-}(X)n - X^{\bullet} + R^{\bullet} \rightarrow Ph\text{-}CO\text{-}O\text{-}(X)n - X - R$$
$$\text{(grafting into)} \quad (3)$$

According to the above equations, the graft copolymer formation will results not from propagation by radicals formed on the cellulose backbone [eq. (1) grafting from] but rather from termination of growing chains of copolymer on the cellulose backbone [eq. (3) grafting into]. With respect to our

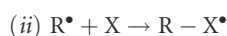**Table III.** Monomer Reactivity Ratio-Values for the Three Investigated Systems

Reactivity ratio	P(AN-S)	P(AN-AA)	P(AN-IA)
r_1	0.149 (AN)	0.556 (AN)	0.317 (AN)
r_2	0.389 (S)	2.254 (AA)	2.091 (IA)

experimental finding, the values of percent efficiency % GE for the three graft copolymerization systems were below 12% in which:
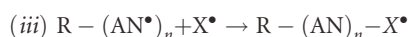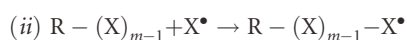
$$\%GE = (\text{The weight of grafted polymer/} \\ \text{The weight of total polymer formed}) \times 100$$

These low values of grafting reactions indicate that a large proportion of the copolymer formed during the grafting reaction was not bounded onto the cellulose backbone which means that the formation of unbound copolymer (free in solution) is faster process [eq. (2) than eqs. (1) or (3)]. Theses results could be explained by the suggestion that the eq. (1) grafting form may be more probable than [eq. (3) grafting into]. Also, the increase of the reaction medium viscosity leads to the difficult movement of the copolymer radicals to reach the reactive sites of the cellulose backbone. On the basis of our experimental findings, suitable reaction steps have been proposed for graft copolymerization of selected comonomers onto cellulosic paper sheet. AN is Acrylonitrile monomer, X is the other monomer (S or AA or IA).
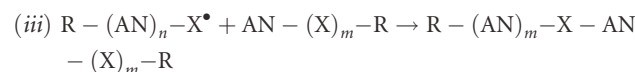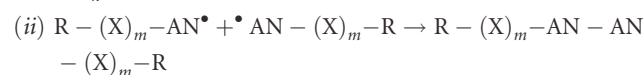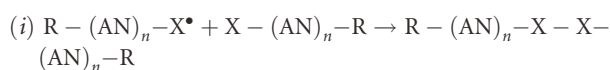
(a) Initiation:

(i) $R^\bullet. + AN \rightarrow R - AN^\bullet$

(ii) $R^\bullet + X \rightarrow R - X^\bullet$

(b) Propagation:

(i) $R - (AN)_{n-1} + AN^\bullet \rightarrow R - (AN)_{n-1} - AN^\bullet$

(ii) $R - (X)_{m-1} + X^\bullet \rightarrow R - (X)_{m-1} - X^\bullet$

(iii) $R - (AN^\bullet)_n + X^\bullet \rightarrow R - (AN)_n - X^\bullet$

(iv) $R - (X)_m + AN \rightarrow R - (X)_m - AN$

(c) Termination:

(i) $R - (AN)_n - X^\bullet + X - (AN)_n - R \rightarrow R - (AN)_n - X - X - (AN)_n - R$

(ii) $R - (X)_m - AN^\bullet + {}^\bullet AN - (X)_m - R \rightarrow R - (X)_m - AN - AN - (X)_m - R$

(iii) $R - (AN)_n - X^\bullet + AN - (X)_m - R \rightarrow R - (AN)_n - X - AN - (X)_m - R$

Termination also can occur as a chain transfer action by solvent H^+ or as a oxidation product in the presence of Fe^{2+} in the reaction medium which can also act as a catalyst. The n and m are the average sequence lengths of AN and (S or AA or IA) blocks, respectively, in the grafted polymer chains. From the data of the monomer reactivity ratio experimental results by Fireman Röss method for the copolymer formed in the reaction

medium (at conversion % less than 10%), it was calculated and the data are summarized in Table III.

a. S-AN Copolymer:
From the above data, it is concluded that $r_{AN} = 0.149 < 1$, $r_s = 0.389 < 1$, $r_{AN}.r_s = 0.0.058 \ll 1$.

In this case there is a tendency for alternation. Also, the statistical distribution of the monomer sequences and content of AN-AN, S-S, and AN-S in copolymer chains were calculated using the following equations[23]

$$X = \Phi_1 - 2\Phi_1(1 - \Phi_1) + \{1 + [(2\Phi_1 - 1)^2 \\ + 4r_1 r_2 \Phi_1(1 - \Phi_1)]^{0.5}\} \quad (1)$$

$$Y = (1 - \Phi_1) - 2\Phi_1(1 - \Phi_1) \\ + \{1 + [(2\Phi_1 - 1)^2 + 4r_1 r_2 \Phi_1(1 - \Phi_1)]^{0.5}\} \quad (2)$$

$$Z = 4\Phi_1(1 - \Phi_1) + \{1 + [(2\Phi_1 - 1)^2 + 4r_1 r_2 \Phi_1(1 - \Phi_1)]^{0.5}\} \quad (3)$$

where r_1 and r_2 are the reactivity ratios of AN and S, respectively; Φ is the molar fraction of AN in the copolymer and X, Y, and Z are the mole fractions of AN-AN, S-S, and AN-S sequence in the copolymer, respectively. The data of AN contents (mol %) in the copolymer were obtained by elemental analysis (N-content) and following eq. (4)

$$\Phi_1 = (1/\{1 + [(14/N) - 53.06]/104.15]\}) \times 100 \quad (4)$$

where N is the nitrogen content (mol %) in copolymer; 53.06 and 104.15 are the molecular weights of AN and styrene, respectively. If the copolymer was prepared with the feed ratio 0.5 : 0.5 for AN/S the nitrogen content was 7.95% (0.0795 mol %), the structural data of the AN-S copolymer at conversion of less than 10% are given in Table IV. Comparing the calculated mole fraction of AN-S sequence in the copolymer, we found that the content of AN-S alternating sequence in the copolymer is as high as ∼80% which confirms that poly(AN-*co*-S) is an alternating copolymer.

b. AN-AA Copolymer:
From the above data, it is concluded that $r_{AN} = 0.556 < 1$, $r_{AA} = 2.254$. In this case the propagation reaction $-M_{AA}-M_{AA}$ and $-M_{AN}-M_{AA}$ will be prepared over $-M_{AA}-M_{AN}$ and $-M_{AN}-M_{AN}$, hence the probability of M_{AA} entering the AN-AA copolymer chain is higher compared to M_{AN}. The copolymer formed will therefore be richer in M_{AA} in random placement

c. AN-IA Copolymer:
The trend in case of AN-IA copolymer is similar to the AN-AA copolymer case $r_{AN} = 0.317 < 1$, $r_{IA} = 2.091 > 1$, indicating

Table IV. Monomer Reactivity Ratio-Values for the Three Investigated Systems

Copolymer composition (mol %)		Sequence distribution (mol %)		
AN	S	An-AN(X)	S-S(Y)	AN-S(Z)
45.8	54.2	3.1	3.6	79.2

Table V. Mean ± Standard Deviation (N=S) of Mechanical Properties for Paper Sheet Before and After Graft Copolymerization Reaction

Paper sheet sample	Tensile strength in machine direction (N/mm^2)	Strength elongation at break in machine direction (%)	Tearing resistance across machine direction (g cm)	Burst strength (N/mm^2)	Degree of brightness (%)
Paper Sheet	9.90 ± 0.02	1.75 ± 0.06	38 ± 2.2	0251 ± 0.02	87.60 ± 4.1
Paper gr-co-AN-S-3h-19%	11.73 ± 0.02	1.98 ± 0.06	45.2 ± 1.7	0.335 ± 0.02	26.30 ± 3.4
Paper gr-co-AN-S-2h-16%	10.90 ± 0.03	1.93 ± 0.06	42.6 ± 2.1	0.303 ± 0.02	28.53 ± 3.4
Paper gr-co-AN-AA-2h-14%	9.34 ± 0.04	1.90 ± 0.02	40.5 ± 2.5	0.321 ± 0.02	29.86 ± 3.3
Paper gr-co-AN-IA-2h-8%	8.53 ± 0.04	1.80 ± 0.02	39.2 ± 2.5	0.265 ± 0.03	40.65 ± 3.4
Paper gr-co-AN-IA-3h-10%	8.19 ± 0.06	1.79 ± 0.06	44.4 ± 1.5	0.257 ± 0.02	39.82 ± 3.4

that the growing acidic comonomer radicals -M_{AA} or -M_{IA} have a greater tendency toward its own monomer unit, therefore the probability of M_{IA} entering the AN-IA copolymer chain is higher as compared to M_{AN} the copolymer will therefore be richer in M_{IN} in random placement.

From the above discussion, it is clear that we can predict the graft copolymer structure by calculation of r_1 and r_2 for each system by the determination of nitrogen content of the formed copolymer in solution less than 10% conversion.

Mechanical Properties

The mechanical properties of the ungrafted and grafted paper sheet with different monomeric pairs are measured as described in the experimental part. The data are summarized in Table V. From the table it is clear that the tensile strength, stretch elongation at break, tearing resistance, and burst strength increase with the grafting of the paper sheet with different monomeric pairs, while the brightness decreases after grafting the paper sheet with different monomeric pairs.
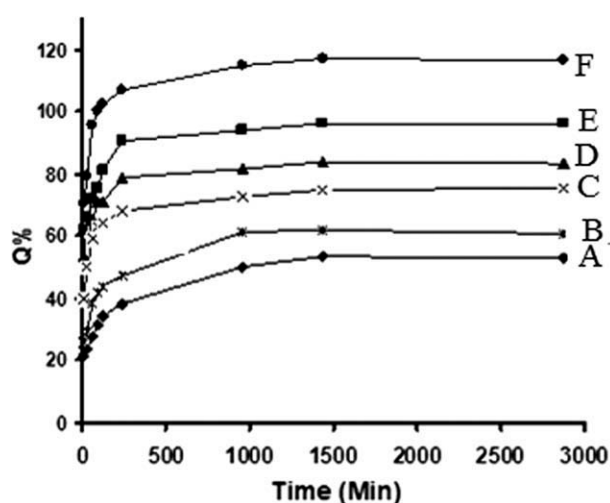
Water Absorption and Water Absorption Capacity of the Paper Sheet Before and After Graft Copolymerization Reaction with Different Monomeric Pairs

Figure 3 shows both water absorption curves at different time intervals up to 48 h and water absorption capacity at equilibrium state. It was confirmed that 24 h equilibration was enough to reach the equilibrium swelling of the samples for paper sheets before and after graft copolymerization reaction with different monomeric pairs; by comprising the samples, any protective effect onto paper can be evaluated. From the figure it can be concluded that for paper grafted by monomers pair (hydrophobic as AN/S or hydrophilic as AN/IA and AN/AA) the quantity of absorbed water and water absorption capacity are always smaller than the ungrafted paper.

The grafted chains in the fiber structure hinder the penetration and the absorption of water molecules onto cellulosic chains, i.e., the grafted chains act as barriers to the penetration of water to the cellulosic fibers of paper by controlling the water absorption capacity (transporting of water from the surface into the bulk of the paper) according to the grafted copolymeric chains on paper sheet as illustrated in scheme represented in Figure 4.

It shown in Figure 2 that in case of grafted paper with the same monomeric pairs, the reduction of water absorption is directly related to the amount of grafted polymer (%) present in the sample.
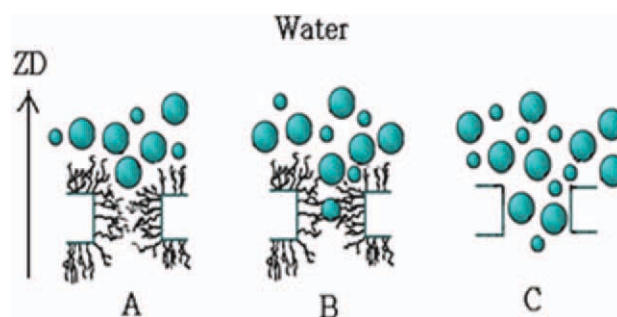

Figure 3. Water absorption curves for paper sheet before and after graft copolymerization reaction; (A) Paper gr-co-AN-S 3h 19%, (B) Paper gr-co-AN-S 2h 16%, (C) Paper gr-co-AN-IA-5h 10%, (D) Paper gr-co-AN-IA-2h 8%, (E) Paper gr-co-AN-AA-2h 14%, (F) Ungrafted paper sheet.

Figure 4. Schematic representation for cross-section of a pore structure and pore function in paper sheet with (A) grafted hydrophobic chains, (B) grafted hydrophilic chains, (C) pure ungrafted paper. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
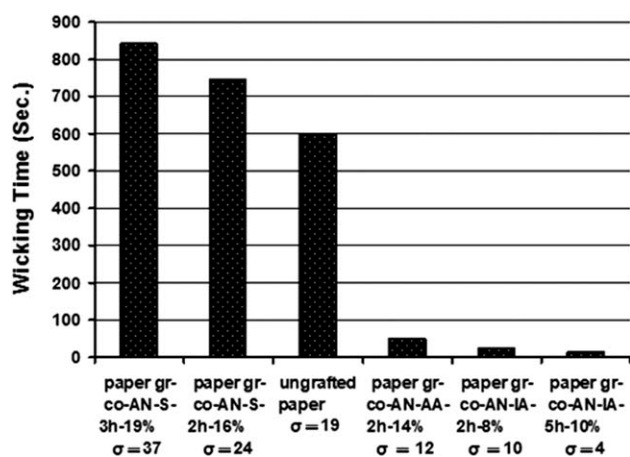
Figure 5. The average wicking time of water into paper sheet before and after graft copolymerization reaction (standard deviation δ at $N = 10$).

The paper gr-*co*-AN-S-3h-19% is less water absorption than the paper gr-*co*-AN-S-2h-16% and the paper gr-*co*-AN-IA-5h-10% is less water absorption than the paper gr-*co*-AN-IA-2h-8%.

Wetting Behavior Measurements for the Paper Sheet Before and After Graft Copolymerization Reaction with Different Monomeric Pairs

The change of the fiber chemical composition leads to the change of its surface wetting because each fiber type has distinct wetting and surface properties.[24] Wettability can be valuable for characterizing the fiber surfaces, liquid transport (interaction of fibers with liquids), and adhesion with polymers.[25]

Figure 5 shows the average wicking time for paper sheet samples before and after graft copolymerization reaction by different monomeric pairs in which water is the wicking liquids. The wicking experiments show good reproducibility, as can be seen by the standard deviation (σ) values of the average wicking times for the different paper samples. The wicking time has the following order:

paper gr-*co*-AN-S-3h-19% > paper gr-*co*-AN-S-2h-16% > ungrafted paper > paper gr-*co*-AN-AA-2h-14% > paper gr-*co*-AN-IA-2h-8%> paper gr-*co*-AN-IA-5h-10%.

The fastest wicking time and consequently high affinity to water "high wettability" can be observed for paper grafted by AN/IA and AN/AA systems, respectively. The slowest wicking time and consequently high resistance to water "poor wettability" can be observed for paper grafted by AN/S system.

Paper strips grafted with AN/S systems are hydrophobic because the AN-S copolymers lower their surface energy. On a macroscopic scale, a surface that is not wetted by a particular liquid has a lower critical surface tension than the surface tension of that liquid. In the case of flat substrates, it is the chemical nature of the functional group packing which governs the surface wettability.

AN-S copolymers covalently bond to the surface of paper and cellulose fibers, creating an abundance of highly grafted AN-S copolymer chains and groups on the surface .The tightly bound, nonbonding electron pairs surrounding each N atom core shell

in N—C bonds are not easily polarized. Therefore hydrogen bonding is hindered and dispersion interactions with polar and nonpolar liquids, respectively.

Therefore, paper grafted by AN/S systems exhibit the high resistance to water, the wicking time is 840.6 s for paper gr-*co*-AN-S-3h-19% and 744 s for paper gr-*co*-AN-S-2h-16%.

In case of ungrafted paper sheet, the wicking time is 595.8 s, it can be assumed that this high wicking time is related to the material which is widely used as internal size in the paper industry to increase paper hydrophobicity as alkyl ketene dimers.

According to the Wakida et al.,[26] the increased surface tension is due to oxygen incorporation. Introducing oxygen elements onto the fiber surface in the form of —OH, C=O, and —COOH can increase hydrophilicity.[27] In case of using AN/IA and AN/AA systems for grafting, we can suggest that the increasing of surface tension of the grafted paper is due to the introduction of polar groups (COOH) from IA and AA, respectively .This increase in surface tension leads to the fastest wicking time and consequently high affinity to water " high wettability" for paper sheet grafted by AN/IA and AN/AA systems. The wicking time for paper gr-*co*-AN-IA-5h-10% is 13.8 s, for paper gr-*co*-AN-IA-2h-8% is 21.6 s and for paper gr-*co*-AN-AA-2h-14% is 51 s. The obtained results are due to the presence of dicarboxylic IA and the mono-carboxylic AA present in the copolymer grafted chains onto paper sheets.

CONCLUSION

The above results reveal the following conclusions:

1. The grammage of the paper sheet increases after graft copolymerization reaction depending on the copolymerization reaction time and the nature of the introduced copolymer.
2. The graft copolymerization reaction of AN with (styrene or AA or IA) comonomers onto paper sheet is established through the infrared spectroscopic analysis on the ungrafted paper sheet and the three grafted products.
3. From the above obtained results of water absorption and surface wettability measurements one can conclude that the graft copolymerization reactions of AN/S monomeric pairs improve the hydrophobicity and the water resistance of the paper sheets.

Therefore, in the specific case of library paper, the retreatment of such materials with suitable monomers by graft copolymerization reaction is to decrease its surface reactivity, wettability, and consequently to decrease its fast damage and to protect library papers against degradation or damage.

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